Background Document
For Chemical Neutralization as a
Land Disposal Restriction Treatment Technology
For Chemical Agent Associated Waste

U.S. Army Dugway Proving Ground
Directorate of Environmental Programs

July 24, 1998

Contract Number DAAD09-94-D-0001

Submitted To:

U.S. Army Dugway Proving Ground
Dugway, UT 84022-5000

Submitted By:

AGEISS ENVIRONMENTAL, INC.

1900 Grant Street, Suite 1130
Denver, CO 80203
And
Analytical Quality Solutions
2112 Deer Run Drive
South Weber, UT 84405

Background Document
For Chemical Neutralization as a
Land Disposal Restriction Treatment Technology
For Chemical Agent Associated Waste

U.S. Army Dugway Proving Ground
Directorate of Environmental Programs

July 24, 1998

Contract Number DAAD09-94-D-0001

Submitted To:

U.S. Army Dugway Proving Ground
Dugway, UT 84022-5000

Submitted By:

AGEISS Environmental, Inc.
1900 Grant Street, Suite 1130
Denver, CO 80203

And

Analytical Quality Solutions
2112 Deer Run Drive
South Weber, UT 84405

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF ABBREVIATIONS AND ACRONYMS

%	Percent
Army	U.S. Army
AsO_3	Arsenic trioxide
$AsCl_3$	Arsenic trichloride
atm-m^3/mol	atmosphere-cubic meter per mole
°C	Degrees Celsius
cal/g	calories per gram
cal/mole	calories per mole
$Ca(OCl)_2$	Calcium hypochlorite (HTH)
CaCl(OCl)	Calcium chloride hypochlorite (STB)
CaO	Calcium oxide
CAS Reg. No.	Chemical Abstract Service Registry Number
CCTF	Combined Chemical Test Facility
ClO_3^-	Chlorate ion
cm^2/s	centimeters squared per second
DESH	2-Diisopropylaminoethanethiol
DIMP	Diisopropylmethylphosphonate
DPG	Dugway Proving Ground
EA2192	S-(2-Diisopropylaminoethyl) methylphosphonothioic acid
EA4196	Bis(2-diisopropylaminoethyl) disulfide
EMPA	Ethylmethylphosphonic acid
EPA	U.S. Environmental Protection Agency
EtOH	Ethanol
F^-	Fluoride ion
ΔG	Change in Free Energy
g/cc	grams per cubic centiliter
g/cm^3	grams per cubic centimeter
g/L	grams per liter
g/mL	grams per milliliter
g/mol	grams per mole
GA	Tabun
GB	Sarin
GD	Soman
GF	Cyclohexylmethyl phosphonofluoridate
ΔH	Heat of Reaction
hr	hour(s)
H	Levinstein Mustard; Sulfur Mustard
HCN	Hydrogen cyanide

HD	Distilled Levinstein Mustard; Distilled Sulfur Mustard
HF	Hydrogen fluoride
HL	Distilled Levinstein Mustard - Lewisite mixture
HN-1	2,2′-Dichlorotriethylamine; Nitrogen Mustard
HN-2	2,2′-Dichlorodiethylmethylamine; Nitrogen Mustard
HN-3	2,2′,2′′-Trichlorotriethylamine; Nitrogen Mustard
H_2O	Water
HQ	75% HD / 25% 1,2-bis(2-chloroethylio) ethane mixture
HT	Distilled Levinstein Mustard (Bis-(2-chloroethylthio))ethyl ether mixture
HTH	Calcium hypochlorite
IMPA	Isopropyl methylphosphonic acid
kcal/mol	kilocalories per mole
K_{eq}	Equilibrium Constant
K_H	Henry's Law Constant
K_{oc}	Soil Organic Carbon/Water Partition
K_{ow}	Octanol/Water Partition Coefficient
L	Lewisite
L-1	2-Chlororovinyldichloroarsine
L-2	Bis-(2-chlorovinyl)chloroarsine
L-3	Tris-(2-chlorovinyl) arsine
LDR	Land Disposal Restriction
mg/L	milligrams per liter
mg/m^3	milligrams per cubic meter
min	minutes
mm Hg	millimeters of mercury
MPA	Methylphosphonic acid
MTF	Materiel Test Facility
NaCN	Sodium cyanide
Na_2CO_3	Sodium carbonate
Na[EMPA]	Sodium salt of ethyl methylphosphonic acid
NaF	Sodium fluoride
Na[IMPA]	Sodium salt of isopropyl methylphosphonic acid
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
Na[PMPA]	Sodium salt of pinacolyl methylphosphonic acid
ND	Not Detected
NH_4OH	Ammonia
NMR	Nuclear Magnetic Ressonance Spectroscopy
NR	Not Recommended

OCl^-	Hypochlorite ion
OH^-	Hydroxide ion
PMPA	Pinacolyl methylphosphonic acid
RCRA	Resource Conservation and Recovery Act
Q	1,2-bis(2-chloroethylthio)ethane
ΔS	Change in Entropy
S_N2	Second-order Nucleophilic Substitution
sec	second(s)
SOP	Standing Operating Procedure
STB	Supertropical Bleach Slurry
T	absolute temberature
TGD	Thickened Soman
UCAR	Utah Chemical Agent Rule
UDSHW	Utah Division of Solid and Hazardous Waste
VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate
Vx	O-ethyl S-[2-(dimethylamino)ethyl] methylphosphonothioate

$\mu g/L$	micrograms per liter

1.0 INTRODUCTION

This Background Document for Chemical Neutralization as a Land Disposal Restriction Treatment Technology for Chemical Agent-Associated Waste is to assist the Land Disposal Restrictions Utah Group established by the Chemical and Biological Defense Command support the Utah Division of Solid and Hazardous Waste (UDSHW) in developing Land Disposal Restriction (LDR) treatment standards. This report summarizes the review of the literature and the performance database to support chemical agent-related waste stream neutralization as a specific LDR technology.

AGEISS Environmental, Inc., with the support of Analytical Quality Solutions, prepared the report in accordance with specifications in Task Order 024 entitled Chemical Agent Waste Management Plan under Dugway Proving Ground (DPG) Contract DAAD09-94-D-0001. Only documents available through the DPG Technical Library and DPG's performance database that contains approximately 1 year of the analytical results of decontaminated chemical agent-related waste streams were reviewed.

The remainder of this introductory section discusses the following topics:

- Regulatory background of chemical neutralization as an applicable treatment technology for LDRs
- Purpose and scope of the report
- Report organization

1.1 REGULATORY BACKGROUND OF CHEMICAL NEUTRALIZATION AS AN APPLICABLE TREATMENT TECHNOLOGY FOR LAND DISPOSAL RESTRICTIONS

The LDRs were mandated for wastes designated as hazardous under the Federal Resource Conservation and Recovery Act (RCRA) program by the 1984 Hazardous and Solid Waste Amendments to RCRA. LDRs are treatment requirements for wastes prior to land disposal. When a waste is determined to be hazardous, it must be treated to comply with specified treatment standards prior to land disposal. These treatment standards substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste (RCRA Section 3004(m)). This section presents the regulatory background for chemical neutralization as an applicable treatment technology for land disposal of decontaminated chemical agent-related wastes.

RCRA was intended by Congress to be a state-implemented program. The U.S. Environmental Protection Agency (EPA) was charged with developing a minimum set of standards for managing hazardous waste under the RCRA program; states would then adopt these regulations and seek authorization from EPA to implement the RCRA program within their boundaries. States cannot be less

stringent than the Federal program in adopting EPA's regulations, however, states can develop regulations that are more stringent.

The State of Utah has been authorized by EPA to operate the RCRA program. UDSHW administers the RCRA program including the LDR program. UDSHW adopted EPA's RCRA characteristics and lists of hazardous wastes. Because Deseret Chemical Depot and DPG have missions associated with chemical agents, the UDSHW modified its regulations under R315-2-11 to add chemical agents and associated wastes as hazardous wastes within the state in July, 1988. In addition, under R315-2-10, UDSHW included residues from demilitarization, treatment, and testing of the chemicals identified in R315-2-11. At that time, no management standards, such as LDR treatment standards, were developed. In February 1995, the UDSHW announced a regulatory initiative to re-examine its current hazardous waste listings for chemical agent wastes and to establish LDR treatment standards for chemical agent wastes as part of the Utah Chemical Agent Rule (UCAR). This initiative is called the proposed rule.

The chemical agent waste streams include agents that become wastes, and wastes that result from treatment of agent. This report assesses the effectiveness of neutralization to treat the various chemical agent waste streams to or below the proposed LDRs identified for the chemical agents. There are two types of LDR treatment standards; technology-based or concentration-based. Where a technology-based standard applies, wastes must be treated by that technology. Where a concentration-based standard applies, wastes must be treated to meet concentrations established for hazardous constituents. The primary advantage of the technology-based standard is that wastes do not need to be analyzed to prove that treatment standards have been met; the primary advantage of the concentration-based standard is that the facility has great latitude to determine the most appropriate technology to apply to treat the waste, including emerging and innovative technologies.

An innovative approach has been established with respect to these standards. Both technology- and concentration-based standards are proposed for the same listed waste streams and both standards are to be established based on risk. The U.S. Army (Army) would be permitted to choose which standard would be applied to specific listed waste streams. Using this approach, protection of human health and the environment is ensured, while repeated and expensive analyses are avoided. Another advantage of this approach is that, when emerging and innovative technologies become available, the rule would permit their use as long as the concentration-based standards are met.

Concentration-based LDR standards have not been finalized at this time. They are being developed by the U.S. Army Center for Health Promotion and Preventative Medicine using U.S. Environmental Protection Agency risk assessment methodology. Chemical agent-related waste streams at DPG are presently being treated to the U.S. Army drinking water standards presented in Table 1.1-1. The drinking water standards are more stringent than the proposed concentration-based LDR standards.

Table 1.1-1 U.S. Army Drinking Water Standards

Chemical Agent	Drinking Water Standard (milligrams per liter)
Tabun (GA)	0.02
Sarin (GB)	0.02
Soman (GD)	0.02
O-ethyl S-[2(diisopropylamino)ethyl] methylphosphonothioate (VX)	0.02
Sulfur Mustard (HD)	0.20
Lewisite (L)	2.0

1.2 PURPOSE AND SCOPE

The purpose of this report is to provide information to support chemical neutralization as an effective LDR treatment technology for chemical agent-related waste streams generated by Army chemical agent operations at DPG.

The scope of this report is limited to review of documents available from the DPG Technical Library and review of DPG data.

1.3 REPORT ORGANIZATION

The remainder of the Background Document for Chemical Neutralization as a Land Disposal Restriction Treatment Technology for Chemical Agent-Associated Waste is organized in the following sections and appendices:

- 2.0 Industry Affected and Waste Characterization - This section introduces the chemical agent-related industry at DPG which uses neutralization as a treatment technology. It provides information concerning the industry affected, including a description of processes at DPG and resulting waste streams, chemical agent properties and reactions, and associated neutralization solutions.

- 3.0 Support for Chemical Neutralization of Chemical Agent Waste Streams as a Land Disposal Restriction Treatment Technology - This section describes products of neutralization of the chemical agents identified in Section 2.0 and presents data to be used in determining if these neutralization procedures are "applicable" and can be considered "demonstrated."

- 4.0 Summary and Conclusions - This section briefly summarizes chemical neutralization procedures, products, and concludes whether there is enough data to consider neutralization procedures as "applicable" and "demonstrated."

- 5.0 References - This section lists those references cited in this report.

- Appendix A - This appendix contains a chemical structures dictionary.

Tables are presented in text as closely to the first reference as possible.

2.0 INDUSTRY AFFECTED AND WASTE CHARACTERIZATION

DPG generates chemical agent-related waste as a result of its mission support activities. DPG's mission includes testing conventional munitions and weapons systems and determining the effects of the chemical warfare agents and neutralization solutions on military equipment and supplies. Section 2.1 identifies DPG as the industry affected, discusses DPG chemical agent related generators and test facilities, and identifies the DPG processes that generate chemical agent-related hazardous waste. Section 2.2 characterizes the chemical agent and chemical agent-related wastes generated at DPG, briefly discusses the neutralization process, and provides a description of chemical agent and associated neutralization solutions.

2.1 INDUSTRY AFFECTED AND PROCESS DESCRIPTION

This section describes the DPG process for generating chemical-agent related waste streams, and includes:

- DPG process description
- DPG chemical agent-related waste streams

2.1.1 Dugway Proving Ground Process Description

DPG generates chemical agent-related waste during fulfillment of its mission which includes developing and testing attack deterrent capabilities, developing and testing methodss to protect personnel and equipment from chemical agent attacks, determining the effects of chemical warfare agents, and neutralization solutions on military equipment and supplies. The majority of the chemical agent-related waste is generated during neutralization of materials involved in chemical agent testing. The remaining chemical agent-related wastes that may be generated at DPG are associated with range-recovered munitions, personal protective equipment, and spilled material and waste. Generators of chemical agent-related waste at DPG are West Desert Test Center and the Directorate of Environmental Programs. Table 2.1-1 presents a summary of the chemical agent-related hazardous wastes generated at DPG.

Table 2.1-1 Summary of Chemical Agent-Related Wastes Generated at Dugway Proving Ground.

Generator	Waste Material
West Desert Test Center	Spent Neutralization Solution
	Neutralized Solid Test Items (Neutralized Debris)
	Mask Filters
	Carbon Ventilation Filters
	Ventilation Duct Work, High Energy Particulate Air Equipment
	Filters and Prefilters
	Range Recovered Munitions
	Personal Protective Equipment
Directorate of Environmental Programs	Spilled Material
	Personal Protective Equipment
	Investigation Derived Waste
	Installation Restoration Program Waste
	Miscellaneous Chemical Agent-related Wastes including spilled wastes

Chemical agent testing is conducted at three sites:

- Building 3445
- Materiel Test Facility (MTF), Building 8027
- Combined Chemical Test Facility (CCTF), Buildings 4156 and 4165

Building 3445 and the MTF are in the vicinity of the Carr Facility and are referred to as the Test Chambers. The CCTF is located in the Ditto Technical Center.

2.1.2 Dugway Proving Ground Chemical Agent-Related Waste Streams

Chemical agent-related wastes generated at the Test Chambers and the CCTF are categorized as follows:

- Spent neutralization solutions - As part of the chemical agent test procedure, or for housekeeping purposes, the equipment, supplies, and small volumes of excess agent are neutralized with a solution appropriate for the chemical agent used during the test. Neutralization solutions react with chemical agents to destroy them. This process is described for each neutralization solution/chemical agent combination in Section 3.1.

- Neutralized solid test items - Solid test items are a variety of solids that become contaminated with chemical agent as a result of the test operations. There are two categories of neutralized solid test items. First, there are those solids that are being directly tested (e.g., mask canisters, filters, mannequins etc.) Second, there are solids which are ancillary to the test operation (e.g., personal protective equipment, expendable

plasticware, glassware, paper towels).

- Other solid wastes - Other solid wastes are generated as part of the normal maintenance operations at the Test Chambers and CCTF. These wastes include construction or maintenance debris, and ventilation system wastes such as prefilters, high efficiency particulate filters, activated carbon filters, plenums and duct work.

Waste streams that are not associated with the chemical agent test procedures include wastes generated as the result of a chemical agent-related spill, a remedial investigation, or installation restoration activities.

2.2 CHEMICAL AGENT CHARACTERIZATION AND CHEMICAL NEUTRALIZATION SOLUTIONS

Chemical agents tested at DPG fall into two categories: nerve agents and blister (vesicant) agents. Each category contains several chemical agents. The list includes the U.S. Army acronyms with their alternate names (Department of the Army Pamphlet 385-61, 1997). Chemical agents tested at DPG are listed in Table 2.2-1 by category.

Table 2.2-1. Chemical Agents Tested at Dugway Proving Ground.

Chemical Agent Category	Chemical Agent Acronym	Alternate Chemical Agent Names
Nerve Agents	GA	Tabun; O-ethyl N,N-dimethylphosphoramidocyanidate
	GB	Sarin; O-isopropylmethylphosphonofluoridate
	GD	Soman; O-pinacolylmethylphosphonofluoridate
	TGD	GD thickened with a polymer
	GF	Cyclohexylmethylphosphonofluoridate
	VX	O-ethyl S-[2-(diisopropylamino)ethyl]methylphosphonothioate
	Vx	O-ethyl S-[2-(dimethylamino)ethyl]methylphosphonothioate
Blister Agents	H	Levinstein Mustard; Sulfur Mustard
	HD	Distilled Levinstein Mustard
	HL	Mustard-Lewisite Mixture
	HT	60% HD and 40% Bis-(2-(chloroethylthio))ethyl ether Mixture
	HQ	75% HD and 25% 1,2-bis(2-chloroethylthio)ethane mixture
	L	Lewisite; Dichloro(2-chlorovinyl)arsine
	HN-1	2,2′-Dichlorotriethylamine; Nitrogen Mustard
	HN-2	2,2′-Dichlorodiethylmethylamine; Nitrogen Mustard
	HN-3	2,2′,2″-Trichlorotriethylamine; Nitrogen Mustard

Seven chemical neutralization solutions are routinely used at DPG (AGEISS, 1997). They can be separated into two categories based upon the type of neutralization reaction. One category of chemical neutralization reactions is oxidation. The hypochlorite bleaches neutralize by oxidation. The other important neutralization reaction is alkaline hydrolysis, which proceeds by the reaction of hydroxide ion with the chemical agents. Alkaline hydrolysis reaction pathways and rates depend upon pH, temperature, and solvent. At an alkaline pH hypochlorite solutions act universally against the nerve agents and HD by providing both oxidation and alkaline hydrolysis (US Army Medical Research Institute of Chemical Defense, 1995). Table 2.2-2 presents the seven chemical agent neutralization solutions routinely used at DPG.

Table 2.2-2. Chemical Neutralization Solutions Routinely Used at Dugway Proving Ground.

Neutralization Solution Category	Neutralization Solution	Neutralization Solution Acronym and Comments
Chlorinated Bleaches (Oxidation Reactions)	A minimum of 5% aqueous sodium hypochlorite	NaOCl in water
	10% Aqueous supertropical bleach Supertropical bleach slurry	STB is calcium chlorohypochlorite [CaCl(OCl)] with some calcium oxide [CaO] present
	10% aqueous high test hypachlorite High test hypochlorite slurry	HTH is calcium hypochlorite [$Ca(OCl)_2$]. HTH contains twice the available chlorine found in STB
Caustics (Alkaline Hydrolysis Reactions)	Caustic alcohol solution 10% NaOH in alcohol	A minimum of 10% sodium hydroxide [NaOH] in an 80/20 mixture of denatured ethanol (EtOH) and water
	A minimum of 10% aqueous sodium hydroxide	NaOH in water
	A minimum of 10% aqueous sodium carbonate	Na_2CO_3 in water
	Concentrated ammonia	NH_4OH

The remainder of this section discusses the following topics:

- Properties and reactions of chemical agents under neutralization conditions
- Chemical neutralization solutions

2.2.1 Properties and Reactions of Chemical Agents Under Neutralization Conditions

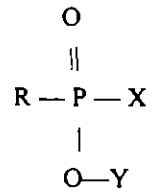
This section describes the properties and reactions of the chemical agents tested at DPG. After some general information about chemical agent properties and reactions, nerve agents and then blister agents

will be discussed. In each chemical agent subsection, the Chemical Abstract Service Registry Number (CAS Reg. No.), and synonyms are listed. Additional CAS Reg. Nos. are listed for some of the chemical agents because some of the chemical agents exist as isomers. In such situations the first CAS Reg. No. applies to the commonly produced mixture of isomers of that agent. The additional CAS Reg. Nos. apply to individual isomers and to other mixtures. Structures for each chemical agent are presented in Appendix A. The chemical reactions pertinent to neutralization are discussed, and tables of environmentally relevant properties, as obtainable, are included.

The chemical agents are reactive molecules by design. They are capable of a variety of different types of chemical reactions under different conditions that may result in different products of reaction. Key reaction conditions for a particular agent may include pH, relative ratios of neutralization solution to agent, the solvent system, the amount of stirring, and/or temperature. The following example demonstrates the effect of the solvent system on the products of reaction. The reaction of VX with hydroxide ion in water produces several products, one of them being a compound called S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA 2192). EA 2192 is formed from VX at medium and high pH. EA 2192 does not break down by further reaction with hydroxide ion. However, experiments with a VX simulant indicate that the same materials (VX + hydroxide ion) reacted in a solution of 90% ethanol (EtOH) would not produce EA 2192 because in EtOH the reaction favors a different reaction pathway. The reaction of distilled Levinstein Mustard (HD) with hydroxide ion is an example of the effect of stirring on the products of reaction. When a large volume of HD was added to 2.5 times its volume of concentrated sodium hydroxide solution and left unstirred for a month, at least 25 compounds formed and some of the HD was left unchanged. However, when HD is stirred with a twenty-fold volume of sodium hydroxide solution it reacts to form thiodiglycol. Chemical neutralization practices therefore include excess sodium hydroxide solution and stirring.

2.2.1.1 General Chemistry of the Nerve Agents

The nerve agents have similar properties because they all contain a phosphorus atom with four substituents around it. The differences between the nerve agents are the result of different substituents around the central phosphorus atom. The tetracoordinated phosphorus atom may be represented generally as follows:

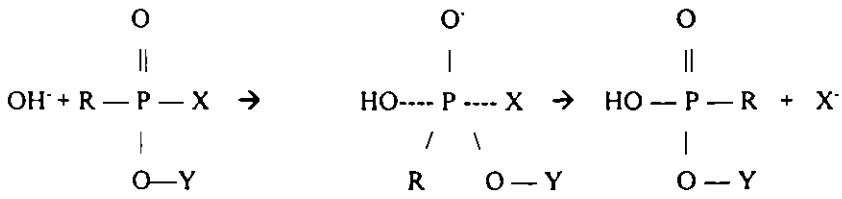


where O is oxygen, and the other substituents are given in Table 2.2-3.

Table 2.2-3. Nerve Agent Substituents.

Chemical Agent	R	Y	X
GA	Dimethylamino group $-N(CH_3)_2$	Ethyl group $-CH_2CH_3$	Cyano group (CN)
GB	Methyl group $-CH_3$	Isopropyl group $-CH(CH_3)_2$	Fluorine (F)
GD	Methyl group $-CH_3$	Pinacolyl group $-CH(CH_3)C(CH_3)_3$	Fluorine (F)
GF	Methyl group $-CH_3$	Cyclohexyl group $-C_6H_{11}$	Fluorine (F)
VX	Methyl group $-CH_3$	Ethyl group $-CH_2CH_3$	N,N-diisopropylmercaptoethyl group $-SCH_2CH_2N(iC_3H_7)_2$

One of the important reactions of the nerve agents is a second-order nucleophilic substitution (S_N2) reaction (also called an addition-elimination reaction) at the tetracoordinate phosphorus (Jody et al., 1983). The nucleophile, an ion with a stronger affinity for the phosphorus atom than one of the other bonded groups, displaces the group with the weakest affinity. In the case of alkaline hydrolysis the hydroxide ion acts as a nucleophile to displace the "X" groups in Table 2.2-3. The S_N2 reaction proceeds through a pentacoordinate intermediate:



In the case of phosphonate esters, of which the nerve agents are an example, the rates of hydroxide ion (OH^-) displacement of the leaving group can be correlated fairly closely with the pKa of the displaced anion (Epstein, J., et al., (1974) cited in Jody, et al., 1983). The correlation of hydrolysis reaction rate with pKa holds up well for the G-agents. It does not apply as well to VX with its multiple reaction pathways (Yang, et al., 1992). S_N2 hydrolysis is the principal neutralization reaction for the G agents, and it is one of the reaction pathways open to VX.

Durst and coworkers (1988) discussed the kinetics of alkaline hydrolysis of the nerve agents in their report. They noted that the rate of hydrolysis in aqueous base will have contributions from water, and from hydroxide reacting with the agent. Because the hydrolysis is an S_N2 reaction, the rate equation will take a second-order form:

$$\text{rate} = k_1[H_2O][\text{agent}] + k_2[OH^-][\text{agent}]$$

Because water is present in large excess and its concentration is not significantly changed by the reaction with agent, the concentration of water behaves like a constant in the rate equation. That allows the equation to be rewritten as:

$$\text{rate} = k_{water}[\text{agent}] + k_{OH}[OH^-][\text{agent}]$$

and factored to become:

$$\text{rate} = (k_{H2O} + k_{OH}[OH^-])\,[\text{agent}]$$

Experimental studies have shown k_{H2O} to be a very small term compared to $k_{OH}[OH^-]$ under the high pH conditions of alkaline hydrolysis. In view of that, the equation can be simplified to the form commonly used to describe the rate of alkaline hydrolysis of the nerve agents:

$$\text{rate} = k_{OH}[OH^-][\text{agent}]$$

Alkaline hydrolysis of the nerve agents commonly is carried out at high pH with an excess of chemical neutralization solution. Thus, for a particular neutralization process the $[OH^-]$ is present in large excess and its concentration is not significantly changed by reaction with the agent. This allows the equation for neutralization at a particular pH to be further simplified by treating $k_{OH}[OH^-]$ as a constant for that pH. Setting $k_{OH}[OH^-] = k_{obs}$, the equation becomes "pseudo first-order":

$$\text{rate} = k_{obs}\,[\text{agent}]$$

One advantage of a first-order reaction is that its half-life which is the time for one-half of the starting material to disappear is independent of concentration and can be calculated from the following equation:

$$t_{1/2} = (\ln 2)/k_{obs} = 0.693/k_{obs}$$

With experimentally determined k_{OH} values for the different nerve agents the rate of neutralization by alkaline hydrolysis can be predicted for those agents at different pH levels. In practice, the rate constants sometimes include a temperature correction term to allow prediction of neutralization rates at different temperatures.

Table 2.2-4 gives the experimentally determined values for k_{OH} for four nerve agents along with the corresponding half-lives at pH = 12 (Durst, et al., 1988).

Table 2.2-4 Half-Lives of Nerve Agents.

Chemical Agent	k_{OH} (M^{-1} sec^{-1})	$t_{1/2}$ (sec) at pH = 12
GA	7.5	9.2
GB	25	3
GD	10	7
VX	0.083	835

According to Table 2.2-4, it would take three seconds to reduce the concentration of GB from 1 mole/liter to 0.5 mole/liter. It also would take three seconds to reduce the concentration of GB from 0.01 mole/liter to 0.005 mole/liter.

In general, the time required for neutralization of an agent by alkaline hydrolysis to a specific level can be estimated using the half-life of the neutralization reaction. A value for the half-life is obtained using the assumptions reviewed in the preceding paragraphs:

- The contribution of water to the hydrolysis process is assumed to be very small in comparision to the contribution of the hydroxide ion

- The hydroxide ion is assumed to be present in such excess that its concentration is not reduced significantly by the neutralization process

The following example is of an "agent" with a molecular weight of 100 and an adequate excess of hydroxide ion. Starting with an initial quantity of 100 grams of chemical agent, 50 grams would be left after one half-life had elapsed. At the end of the second half-life 25 grams would remain. The quantity remaining after "n" half-lives is given by the relationship:

$$\text{Quantity Remaining} = (\text{Initial Quantity})/2^n = 100/2^n$$

Table 2.2-5 tracks the amount of "agent" remaining through ten half-lives with values for 15 and 20 half-lives as well (Durst, et al., 1988).

Table 2.2-5 Quantity of Chemical Agent Remaining After the Specified Number of Half-lives.

Initial Quantity (grams)	Half-Lives	Quantity Remaining (grams)	% Destroyed
100	0	100	0
100	1	50	50
50	2	25	75
25	3	12.5	87.5
12.5	4	6.25	93.75
6.25	5	3.125	96.875
3.125	6	1.5625	98.4375
1.5625	7	0.78125	99.21875
0.78125	8	0.390625	99.609375
0.390625	9	0.1953125	99.804687
0.1953125	10	0.0976562	99.902343
0.0061035	15	0.0030517	99.996946
0.0001907	20	0.0000953	99.999899

It can be seen that exposure to neutralization solution for 10 half-lives achieves 99.9% destruction of agent, while exposure for 20 half-lives achieves 99.9999% destruction.

2.2.1.2 General Chemistry of the Blister Agents

The blister agents (vesicants) neutralized at DPG fall into three categories: the sulfur mustards (H/HD, HT, and HQ), the nitrogen mustards (HN-1 and HN-3), and Lewisite. They have similar properties because they are lipid soluble and because of the structural relationship between the chlorine atom(s) and the neighboring hetero-atom; sulfur, nitrogen or arsenic. In the commonly used blister agents the chlorine atoms are separated from the hetero-atom by two carbon atoms. However, the relationship between structure and vesicancy is not simple. For example, mustard with the formula $(ClCH_2CH_2)_2S$ is a potent blister agent while the disulfide, $(ClCH_2CH_2)_2S_2$, and higher polysulfides, $(ClCH_2CH_2)_2S_x$, are much less potent.

The neutralization of blister agents also is complicated. The hydrolysis of HD is highly dependent upon the reaction conditions. Under ideal conditions (a large excess of water, high pH, and adequate stirring) HD can be hydrolyzed almost exclusively to thiodiglycol and chloride ion. Departure from those conditions can result in a variety of reaction products (Rosenblatt, et al., 1995). For that reason hydrolysis is not recommended for the neutralization of the sulfur mustards. The pH plays an important role in determining the products from the hydrolysis of the nitrogen mustards (Yurow and Davis, 1982) and of Lewisite (Durst, et al., 1988). The nitrogen mustards and Lewisite can be neutralized successfully by alkaline hydrolysis at a sufficiently high pH. Because of the difficulties with hydrolysis of the sulfur mustards, hypochlorite oxidation is the neutralization process commonly used for that group. Yurow and Davis (1982) have stated that the stoichiometry of the hypochlorite oxidation of HD is indefinite because of the many products formed. An excess of hypochlorite is necessary for complete reaction. Significant

heat is produced during the reaction (Yurow and Davis, 1982). J. B. Samuel and co-workers (1998) recently found that a mole ratio of 1:5 to 1:14 for HD:hypochlorite is necessary to complete the neutralization process. The outcome also depends upon the pH.

In summary, the physiological action and neutralization of the blister agents do not fit a straightforward pattern. The sulfur mustards (H/HD, HT, and HQ) have some common characteristics as do the nitrogen mustards (HN-1 and HN-3). Otherwise, it is necessary to consider the blister agents individually.

2.2.1.3 GB (Sarin)

CAS Reg. No.: 107-44-8 (also 50642-23-4, 6171-93-3, 6171-94-4)

Synonyms:
Methyl-isopropyl ester phosphonofluoridic acid
Methyl-1-methylethyl ester phosphonofluoridic acid
Isopropyl methylphosphonofluoridate
Isopropyl ester of methylphosphonofluoridic acid
Methylisopropoxyfluorophosphine oxide
Isopropyl methylfluorophosphonate
O-Isopropyl methylphosphonofluoridate
Isopropyl ester methylfluorophosphonic acid
Isopropoxymethylphosphonyl fluoride
Zarin
EA1208

Properties:
GB is fairly volatile, and therefore is a relatively nonpersistent nerve agent. It evaporates at about the same rate as water (Field Manual 3-9, 1990). Table 2.2-6 summarizes additional environmentally relevant data concerning GB (Rosenblatt, et al., 1995).

Table 2.2-6. Environmentally Relevant Properties of GB.

Property	Data	Data Quality	Reference
Empirical Formula	$C_4H_{10}FO_2P$	Not Applicable	
Molecular Weight	140.1 g/mol	Not Applicable	
Liquid Density	1.0887 g/mL at 25°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Melting Point	-56.9°C	Fair	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Boiling Point	157.8°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Heat of Vaporization	80.66 cal/g	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Vapor Pressure (torr)	2.94/25°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{ow}	0.15 (2)	Poor	Britton and Grant, 1988, cited in Rosenblatt, et al., 1995
Aqueous Solubility (g/L)	Miscible in all proportions.	Good	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	4.0×10^{-7}/25°C	Poor	Preston and Starrock, 1993, cited in Rosenblatt, et al., 1995
Diffusion Coefficient (air)	0.061 cm^2/s at 25°C	Fair	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{OC}	0.45 1.8	Poor Not Available	Rosenblatt, et al. (1995) Small, 1984, cited in Rosenblatt, et al., 1995

Reactions:

GB is infinitely soluble in water and will hydrolyze under acidic, neutral, and basic conditions. The rate of hydrolysis is slowest in the pH range 4 to 6. It has a hydrolytic half-life of about 160 hours at pH 5 and 25 degrees Celsius (°C). The rate of hydrolysis becomes more rapid below pH 4 and above pH 6, increasing rapidly with increasing hydroxide ion concentration. When large amounts of GB are added to distilled water, the observed hydrolysis rate first decreases but increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect (Clark 1989, cited in Rosenblatt, et al., 1995). The second-order rate constant for the hydroxyl ion catalyzed hydrolysis of GB is:

$$\log k_2\ (M^{-1}\ min^{-1}) = 9.8507 - (1{,}985.4/T_K)$$

At 25 °C and at pH 10 the half life of GB is 5 minutes (Demek, et al., 1970, cited by Rosenblatt, et al., 1995).

The alkaline hydrolysis products of GB are fluoride ion and the sodium salt of isopropyl methylphosphonic acid (IMPA).

$$GB + 2\ NaOH \rightarrow Na[IMPA] + NaF + H_2O$$

where: Na[IMPA] is the sodium salt of IMPA

The heat of reaction (enthalpy) is -44.4 kilocalories per mole (kcal/mol) (Davis, et al., 1979). Thermodynamic calculations predict substantially complete conversion of GB to IMPA. The calculated equilibrium constant is log K_{eq} = 21.9 based upon a free energy of -30,000 cal/mol. Nuclear magnetic resonance spectroscopy (NMR) data confirm that IMPA is the sole phosphorus-containing product of the alkaline hydrolysis of GB down to 0.5% (Durst, et al., 1988).

When GB is neutraiized with 5.25% NaOCl in water, the reaction is an alkaline hydrolysis and the products are the sodium salt of IMPA and flouride ion (Durst, et al., 1988). The second-order rate constant for this reaction is larger (10 M^{-1} sec^{-1} at 25°C) than that for hydrolysis with OH^-. This is attributed to the catalytic effect of hypochlorite (OCl) upon the reaction. When large amounts of GB are neutralized with hypochlorite, additional hydroxide must be added to the hypochlorite solution to maintain the pH (Yurow and Davis, 1982).

Because of the sensitivity of GB to hydrolysis there has been a problem with it decomposing in munitions. N,N'-diisopropylcarbodiimide and/or tributylamine have been added as stabilizers. Up to 0.5% of the starting material, methylphosphonic difluoride, and some diisopropylmethylphosphonate (DIMP), an impurity, also may be present in weapons grade GB. The N,N'-diisopropylcarbodiimide hydrolyzes to N,N'-diisopropyl urea (Rosenblatt, et al., 1995). Tributylamine is unaffected by aqueous hydroxide. Methylphosphonic difluoride hydrolyzes rapidly at high pH to form the ions of methylphosphonic acid (MPA) and flouride. The dialkyl ester, DIMP, undergoes slow hydrolysis at high pH to form the monoalkyl ester, isopropylmethylphosphonic acid. Similar stabilizers and impurities may be associated with the other G-agents (Rosenblatt, et al., 1995).

2.2.1.4 GA (Tabun)

CAS Reg. No.: 77-81-6 (also 93957-08-5, 93957-09-6)

Synonyms:
Ethyl N,N-dimethylphosphoramidocyanidate
Ethyl dimethylplosphoramidocyanidate
Dimethylaminoethoxy-cyanophosphine oxide
Dimethylamidoethoxyphosphoryl cyanide
Ethyl dimethylaminocyanophosphonate
Ethyl ester of dimethylphosphoroamidocyanidic acid
Ethyl phosphorodimethylamidocyanidate
EA1205

Properties

Table 2.2-7 presents the environmentally relevant properties of GB (Field Manual 3-9, 1990). The data quality of these properties has not been evaluated.

Table 2.2-7. Environmentally Relevant Properties of GA.

Property	Data	Reference
Empirical Formula	$C_5H_{11}N_2O_2P$	Field Manual 3-9, 1990
Molecular Weight	162.13 g/mol	Field Manual 3-9, 1990
Liquid Density	1.073 g/mL at 25°C	Field Manual 3-9, 1990
Melting Point	-50°C	Field Manual 3-9, 1990
Boiling Point	240°C 220°C to 246°C/760 mm Hg	Material Safety Data Sheet for GA Field Manual 3-9, 1990
Heat of Vaporization	79.56 cal/g	Field Manual 3-9, 1990
Vapor Pressure	0.037mm Hg at 20°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility	9.8% at 25°C 7.2% at 20°C	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	858 mg/m^3 at 30°C 610 mg/m^3 at 25°C 328 mg/m^3 at 20°C 90 mg/m^3 at 0°C	Field Manual 3-9, 1990

Reactions:

The reaction of GA is similar to that of GB, GD, and GF. GA is reacted with an excess of OH^- in water to produce the anion of ethyl dimethylaminophosphonic acid and cyanide ion. The equation for the reaction of GA with NaOH is:

$$GA + 2\ NaOH \rightarrow Na[\text{ethyl dimethylaminophosphonate}] + NaCN + H_2O$$

where: Na[ethyl dimethylaminophosphonate] is the sodium salt of ethyl dimethylaminophosphonic acid
NaCN is sodium cyanide

The pseudo first-order rate constant for the hydrolysis of GA by hydroxide ion has been reported as 0.02 min^{-1} at pH 9.5 and 25°C. The associated heat of reaction has been reported as -10.1 kcal/mole. Under acidic conditions the hydrolysis of GA produces dimethylamine (Yurow, 1988). NMR has confirmed the disappearance of GA and the appearance of the anion of ethyl dimethylaminophosphonic acid (Durst, et al., 1988). When sufficient quantities of GA are neutralized using aqueous hydroxide, it becomes necessary to destroy the cyanide ion that is produced to prevent formation of hydrogen cyanide (HCN) if

the solution is acidified. After neutralization is complete treating the solution with hypochlorite will convert the cyanide to nitrogen gas and carbonate ion (Yurow and Davis, 1988).

$$2\ NaCN + 5\ NaOCl + 2\ NaOH \rightarrow N_2 + 2\ Na_2CO_3 + 5\ NaCl + H_2O$$

Alternatively, GA can be neutralized using a solution of hypochlorite. Both the cyano group and the dimethylamino group are lost, producing the ethyl ester of phosphonic acid. The report did not identify the other products of the products of the reaction (Durst, et al., 1988). Dimethyl amine may be a product.

2.2.1.5 GD (Soman)

CAS Reg. No.: 96-64-0 (also 22956-47-4, 22956-48-5)

Synonyms:
Pinacolyl methylphosphonofluoridate
EA1210

Properties:
GD has a solubility of 2.1% in water at 20° C, significantly less soluble than GB. GD is a less volatile, and therefore a more persistent, agent than GB. It evaporates at about one-fourth the rate of water (Field Manual 3-9, 1990). Table 2.2-8 presents additional environmentally relevant data concerning GD (Rosenblatt, et al., 1995).

Table 2.2-8. Environmentally Relevant Properties of GD.

Property	Data	Data Quality	Reference
Empirical Formula	$C_7H_{16}FO_2P$	Not Applicable	
Molecular Weight	182.18 g/mol	Not Applicable	
Liquid Density	1.0223 g/mL at 25°C	Good	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
Melting Point	-42°C	Fair	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
Boiling Point	197.8°C	Good	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
Heat of Vaporization	72.5 cal/g	Good	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
Vapor Pressure (torr)	0.40/25°C 0.274/20°C	Good Good	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995 Material Safety Data Sheet for GA
Log K_{ow}	1.02 1.79 1.60	Poor Not Available Not Available	Britton and Grant, 1988, cited in Rosenblatt, et al., 1995 Rosenblatt, et al., 1995 Rosenblatt, et al., 1995
Aqueous Solubility	34 g/L at 0°C 21 g/L at 20°C	Fair Fair	Edgewood Arsenal, 1974, cited in Rosenblatt, et al., 1995 Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
K_H (atm-m^3/mol)	3.1 x 10^{-6}/20°C	Poor	Rosenblatt, et al., 1995
Diffusion Coefficient (air)	0.047 cm^2/s at 25°C	Fair	Samuel, et al., 1983 cited in Rosenblatt, et al., 1995
Log K_{OC}	1.17	Poor	Rosenblatt, et al., 1995

Reactions:

The hydrolytic half-life of GD is longest in the pH range of 4 to 7, about 144 hours at pH 5 and 20°C. The rate of hydrolysis increases in more alkaline or more acidic solutions. When large amounts of GD are added to distilled water, the observed hydrolysis rate first decreases but increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect (Clark, 1989, cited in Rosenblatt, et al., 1995). The observed hydrolysis rate constant at 25°C, exclusive of buffer effects, is:

$$k_{obs}\ (h^{-1}) = 0.0047 + 33\ [H3O^+] + 5x10^4\ [OH^-]$$ (Healy, 1948, cited in Rosenblatt, et. al., 1995)

The half-life of GD in excess 5% aqueous sodium hydroxide is 0.08 hr at 20° C. The heat of reaction is estimated to be similar to that of GB (-44.4 kcal/mole) because fluorine is the leaving group in both cases (Yurow, 1988). The alkaline hydrolysis of GD produces the anion of pinacolyl methylphosphonic acid (PMPA) and flouride ion. NMR data confirm that the anion of PMPA is the sole phosphorus-containing product of the alkaline hydrolysis of GD down to 0.5% (Durst, et al., 1988).

$$GD + 2NaOH \rightarrow Na[PMPA] + NaF + H_2O$$

where: Na[PMPA] is the sodium salt of PMPA.

Because GD is comparatively insoluble in water the use of a solvent mixture consisting of a small proportion of water and a large proportion of methanol (or another alcohol) can increase the solubility, and therefore the effective rate of neutralization. The alcohol in solution does not significantly inhibit the reactivity of GD or the other G-agents with hydroxide ion. The solution of hydroxide in methanol forms methoxide ion. The methoxide ion also reacts as a nucleophile to attack the central phosphorus atom to form the ester, methyl pinacolyl methylphosphonate. This ester eventually undergoes hydrolysis to form PMPA and perhaps some methyl methylphosphonic acid (Rosenblatt, et al., 1995).

When GD is neutralized with 5.25% NaOCl in water, the reaction is an alkaline hydrolysis and the products are the anion of pinacolyl methylphosphonic acid and fluoride ion (Durst, et al., 1988). Though the rate constant for this reaction has not been determined, it is expected to be similar to that for the analogous GB reaction (Rosenblatt, et al., 1995).

2.2.1.6 TGD

CAS Reg. No.: Not Available.

Synonyms: None.

Properties:
TGD is GD thickened with a polymer. UCON 75-H-90,000 is a polyethylene glycol derivative that has been used to thicken GB, a related G-agent (Angelotti, et al., 1955). Thickeners are added to GD to increase persistence in the field. In general, thickened agents form large droplets that provide a greater concentration reaching the ground and a greater contact hazard than the unthickened forms (Field Manual 3-9, 1990). The environmentally relevant properties of TGD are the same as GD.

Reactions:
Yang and coworkers (1992) have noted that an organic solvent often is added to an aqueous neutralization solution to improve solubility of thickened agents. The neutralization reaction remains the same for the thickened agent after it is in solution. However, many of the oxidation and substitution reactions become slower as the solvent polarity decreases.

2.2.1.7 GF

CAS Reg. No.: 329-99-7

Synonyms:
Cyclohexylmethylphosphonofluoridate
O-cyclohexyl-methylfluorophosphonate
EA 1212

Properties:
The nerve agent, GF, is a slightly volatile liquid, approximately 20 times more persistent than GB. It is almost insoluble in water. Table 2.2-9 presents the environmentally relevant properties of GF (Field Manual 3-9, 1990). The quality of the data are unavailable for the properties of GF.

Table 2.2-9. Environmentally Relevant Properties of GF.

Property	Data	Reference
Empirical Formula	$C_7H_{14}FO_2P$	Field Manual 3-9, 1990
Molecular Weight	180.2 g/mol	Field Manual 3-9, 1990
Liquid Density	1.1327 g/mL	Field Manual 3-9, 1990
Melting Point	-30°C	Field Manual 3-9, 1990
Boiling Point	239°C	Field Manual 3-9, 1990
Heat of Vaporization	90.5 cal/g	Field Manual 3-9, 1990
Vapor Pressure	0.044 mm Hg at 20°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility	0.37% at 20°C	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	438 mg/m^3 at 20°C 581 mg/m^3 at 25°C	Field Manual 3-9, 1990

Reactions:
Little information concerning reactions of GF was found. Based upon similarities in structure to GB and GD, it is expected to hydrolyze rapidly in alkaline solution according to the reaction:

$$GF + 2\ NaOH \rightarrow Na[\text{cyclohexyl methylphosphonate}] + NaF + H_2O$$

where: Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid

By comparison to GB and GD, the reaction is expected to be exothermic and at pH 12 its half-life is expected to be in the range of the half-lives of GB (3 seconds) and GD (7 seconds) at that pH.

2.2.1.8 VX

CAS Reg. No.: 50782-69-9 (also 65143-05-7, 65167-63-7, 65167-64-8)

Synonyms:
Methyl-S-(2-bis(1-methylethylamino)ethyl) O-ethylphosphonothioic acid
O-ethyl-S-(2-diisopropylaminoethyl) methylphophonothioate
S-2-diisopropylaminoethyl O-ethyl methylphosphonothioate
S-2 (2-diisopropylamino)ethyl O-ethyl methylphosphonothioate
O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothioate
O-ethyl-S-(2-diisopropylaminoethyl) methylthiolphosphonate
EA 1701
TX60

Properties:
VX is more persistent than the G-agents because of its lower vapor pressure. Its evaporation rate is about 1/1,500 that of water (Field Manual 3-9, 1990).

Table 2.2-10 presents the environmentally relevant properties of VX (Rosenblatt, et al., 1995).

Table 2.2-10. Environmentally Relevant Properties of VX.

Property	Data	Data Quality	Reference
Empirical Formula	$C_{11}H_{26}NO_2PS$	Not Applicable	
Molecular Weight	267.38 g/mol	Not Applicable	
Liquid Density	1.0083 g/mL at 25°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Melting Point	-50°C	Fair	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Boiling Point	298.4°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Heat of Vaporization	80.8 cal/g	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Vapor Pressure (torr)	6.2×10^{-4}/25°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{ow}	2.36 (Estimate) 2.09 (Estimate) 1.992 (Estimate)	Poor Poor Poor	Britton and Grant, 1988, cited in Rosenblatt, et al., 1995. Small, 1984, cited in Rosenblatt, et al., 1995. Sage and Howard, 1989, cited in Rosenblatt, et al., 1995.
Aqueous Solubility	30 g/L at 25°C	Fair	Edgewood Arsenal, 1974, cited in Rosenblatt, et al., 1995
K_H (atm-m^3/mol)	7.2×10^{-9}/25°C	Poor	Rosenblatt, et al., 1995
Diffusion Coefficient (air)	0.034 cm^2/s at 25°C	Fair	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{oc}	1.18 2.5	Poor Not Available	Sage and Howard, 1989, cited in Rosenblatt, et al., 1995. Small, 1984, cited in Rosenblatt, et al., 1995.

Reactions:

VX hydrolysis rates are slower than those of the G-agents. For example, at pH 10 and 25°C the half-life of VX in water is 40.5 hours (Epstein, et al., 1974, cited in Rosenblatt, et al., 1995) compared to 5 minutes for GB. The same source reported a half-life of 2.5 hours for the hydrolysis of VX in water at pH 12 at 25° C. At pH 5 and 25°C the half-life of VX in water is 2,342 hours compared to 160 hours for GB. (Clark, 1989, cited in Rosenblatt, et al., 1995).

VX is not subject to acid catalyzed hydrolysis but does undergo water-mediated and hydroxyl ion-catalyzed hydrolysis. The hydrolysis of VX proceeds by multiple pathways and results in a more complex set of products than the hydrolysis of the G-agents. Across the pH range the P–S bond is cleaved to give two primary products: ethylmethylphosphonic acid (EMPA) and 2-diisopropylaminoethanethiol (DESH). Bis(2-diisopropylaminoethyl) disulfide (EA 4196) is formed by air oxidation of DESH (Small, 1984, cited in Rosenblatt, et al., 1995). In the middle and higher pH ranges additional reaction pathways contribute to the mix of hydrolysis products. In addition to P–S bond cleavage, the P–O–C bond to the ethoxy group and the C–S bond also are broken (Epstein, et al., 1974, cited by Rosenblatt, et al., 1995). The product of ethoxy group cleavage, EA 2192, is comparatively stable towards hydrolysis (Sage and Howard, 1989, cited in Rosenblatt, et al., 1995). Yang and coworkers (1992) demonstrated that up to 13% percent EA 2192 formed during the hydrolysis of VX even in aqueous 0.1 M NaOH. Szfraniec and coworkers confirmed that 17% EA 2192 formed in aqueous 2.0 M NaOH (1993, cited in Rosenblatt, et al., 1995). Finally, C–S bond cleavage in the neutral pH range results in the formation of O-ethyl methylphosphonothioic acid, diisopropylaminoethyl sulfide and possibly other minor products (Epstein, et al., 1974, and Yang, et al., 1990 cited in Rosenblatt, et al., 1995).

The NMR data presented by Durst and coworkers (1988) show the formation of EA 2192 from VX in 10% alcoholic sodium hydroxide.

The neutralization of VX also is complicated by its low solubility in water. It is a weak acid and therefore less soluble at higher pH, the region of faster reactions. At lower (more acidic) pH the protonated form of VX is more soluble, but the reaction rate with water is much slower (Rosenblatt, et al., 1995). The neutralization of VX has been investigated in a solution of 2 M NaOH with 10% isopropanol added to improve the solubility of VX. A 0.05 M solution of VX formed 22% EA 2192 under those conditions (Yang, et al., 1990 cited in Rosenblatt, et al., 1995).

Further studies of the alkaline hydrolysis of a VX simulant (O, S-diethyl methylphosphonothioate) in very high concentrations of alcohol indicate that such solutions favor P–S bond cleavage rather than P–O–C bond cleavage. From this work with the simulant it is inferred that VX could be neutralized rapidly without forming EA 2192 in strongly basic solutions of methanol or propanol that contain less than 10%

water. This effect has been attributed to the hydrolysis of VX by the preponderance of alkoxide ion present, and not to the decreased solvent polarity (Yang, et al., 1993b cited in Rosenblatt, et al., 1995).

Because of the sensitivity of VX to hydrolysis there has been a problem with it decomposing in munitions. N,N′-diisopropylcarbodiimide or N,N′-dicyclohexylcarbidiimide have been added as stabilizers to weapons grade VX (Rosenblatt, et al., 1995). Hydrolysis converts these stabilizers to N,N′-diisopropylurea or N,N′-dicyclohexylurea, respectively (Rosenblatt, et al., 1995).

The products of the reaction of aqueous hypochlorite with VX vary with pH. At low pH hypochlorous acid reacts with chloride ion to form chlorine:

$$HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$$

Also, at low pH the VX is protonated on the nitrogen, enhancing its solubility:

$$VX + H^+ \rightarrow VXH^+$$

The chlorine reacts with the protonated VX to form EMPA and a sulfonic acid:

$$VXH^+ + 3\ Cl_2 + 4\ H_2O \rightarrow EMPA + Diisopropyltaurine + 6\ HCl + H^+$$

This reaction is thought to proceed in two steps. First the sulfur atom is oxidized then the P–S bond is cleaved by hydrolysis to yield the products (Yang, et al., 1992, cited in Rosenblatt, et al., 1995).

At higher pH the nitrogen atom in VX is not protonated. The OCl^- is thought to attack the available nitrogen, forming an N-oxide, then go on to oxidize the sulfur atom (Yang, et al., 1992). However, the reactions of hypochlorite with VX in basic solution have not been defined completely. Durst noted the possibility of toxic products forming at a pH below 11. With sufficient excess hypochlorite, the stoichiometry of the reaction has been reported as the following equation by Durst and coworkers (1988).

$$VX + 9\ OCl^- + 7\ OH^- \rightarrow EMPA + Diisopropyl\ amine + 9\ Cl^- + 5\ H_2O + SO_4^{-2} + 2\ CO_3^{-2}$$

2.2.1.9 Vx ("V sub x")

CAS Reg. No.: 20820-80-8

Synonyms:
O-Ethyl-S-2-dimethylaminoethyl methylphosphonothioate
EA 1699

Russian VX

Properties:

Vx, called "V sub x", is a V-agent with properties similar to VX. It is nearly ten time more volatile than VX, yet more persistent than the G-agents. The limited information available on this compound is presented in Table 2.2-11. Some of the values are calculated (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-11. Environmentally Relevant Properties of Vx.

Property	Data	Reference
Empirical Formula	$C_7H_{18}NO_2PS$	
Molecular Weight	211.2 g/mol	Field Manual 3-9, 1990
Liquid Density	1.062 g/cc at 25° C	Field Manual 3-9, 1990
Melting Point	Not Available	Not Available
Boiling Point	256° C (approximate)	Field Manual 3-9, 1990
Heat of Vaporization	67.2 cal/g	Field Manual 3-9, 1990
Vapor Pressure	0.0042 mm Hg at 20° C 0.0066 mm Hg at 25° C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility	Slightly soluble in water.	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	48 at 20° C 75 mg/m^3 at 25° C	Field Manual 3-9, 1990

Reactions:

The neutralization reactions of Vx are expected to be similar to those of VX (Field Manual 3-9, 1990).

2.2.1.10 H/HD (Sulfur Mustard)

CAS Reg. No.: 505-60-2

Synonyms:

Bis (2-chloroethyl) sulfide
Bis (beta-chloroethyl) sulfide
1-Chloro-2 (beta-chloroethylthio) ethane
Beta, beta′ - dichlorodiethyl sulfide
2,2′-Dichlorodiethyl sulfide
Di-2-chloroethyl sulfide
Beta, beta′ - dichloroethyl sulfide

2,2' - Dichloroethyl sulfide
EA 1033
Iprit
Kampstoff "Lost"
Lost
Mustard Gas
Senfgas
S-lost
Sulphur Mustard Gas
S-yperite
Yellow Cross Liquid
Yperite

Properties:
The two common mustard agents are:

- H - Levinstein Mustard - 70% bis(2-chloroethyl) sulfide with 30% sulfur-based impurities
- HD - Distilled Mustard - bis (2-chloroethyl) sulfide

H was synthesized for military use mainly by the Levinstein process. In its simplest form the Levinstein process is a reaction between sulfur monochloride and ethylene to produce mustard and elemental sulfur:

$$S_2Cl_2 + 2\ CH_2{=}CH_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl + S$$

This reaction is complicated by the fact that most of the elemental sulfur reacts to form a variety of polysulfides. The Levinstein process produces mustard in a 70% yield, with the proportions of sulfur and the polysulfide impurities depending upon reaction conditions (Rosenblatt, et al., 1995).

The sulfur impurities gave H a distinct odor. They also lowered its freezing point a few degrees, but caused problems with storage. Therefore, a purification process consisting of washing and vacuum distillation was used to produce HD from H (Field Manual 3-9, 1990). It has not been possible to find a listing for the composition of a "typical" sample of H. Such a listing may not be available. Rosenblatt and coworkers (1995), reported the results from analyzing the mustard from two old H munitions and a storage container of HD. Because HD is distilled from H, the two mustards are often referred to as H/HD, particularly when discussing properties and reactions.

HD has a low solubility in water and a low rate of solution. Once the HD is dissolved in H_2O, though, it hydrolyzes rapidly. The hydrolysis of mustard proceeds via an S_N1 mechanism, very likely through a cyclic sulfonium ion intermediate (Yang, et. al., 1992).

Table 2.2-12 presents the environmentally relevant properties of HD (Rosenblatt, et al., 1995).

Table 2.2-12. Environmentally Relevant Properties of HD.

Property	Data	Data Quality	Reference
Empirical Formula	$C_4H_8Cl_2S$	Not Applicable	
Molecular Weight	159.08 g/mol	Not Applicable	
Liquid Density	1.2685 g/mL at 25°C	Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Melting Point	14.445°C	Good	Penski, 1993, cited in Rosenblatt, et al., 1995
Boiling Point	217.5°C	Good	Samuel. et al., 1983, cited in Rosenblatt, et al., 1995
Heat of Vaporization	94.3 cal/g	Good	Samuel. et al., 1983, cited in Rosenblatt, et al., 1995
Vapor Pressure (torr)	0.082/22°C 0.1059/25°C	Good Good	Samuel, et al., 1983, cited in Rosenblatt, et al., 1995 Samuel, et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{ow}	1.37 2.026	Good Fair	Rosenblatt, et al., 1995 Sage and Howard, 1989, cited in Rosenblatt, et al., 1995
Aqueous Solubility	0.92 g/L at 22°C	Fair	Edgewood Arsenal, 1974, cited in Rosenblatt, et al., 1995
K_H (atm-m^3/mol)	1.87×10^{-5} 2.57×10^{-5}	Fair Fair	Rosenblatt, et al., 1995 Sage and Howard, 1989, cited in Rosenblatt, et al., 1995
Diffusion Coefficient (air)	0.060 cm^2/s at 25°C	Fair	Samuel. et al., 1983, cited in Rosenblatt, et al., 1995
Log K_{OC}	2.0-2.1	Poor	Sage and Howard, 1989, cited in Rosenblatt, et al., 1995

Reactions:

The nature of the hydrolysis products of HD is highly dependent upon the reaction conditions. Under ideal conditions (a large excess of water, high pH, and adequate stirring) HD can be hydrolyzed almost exclusively to thiodiglycol and chloride ion (Rosenblatt, et al., 1995). With a HD to water ratio of 1 to 2.5 and a high pH, 1,4-oxathiane, 1,4-dithiane, 2-vinylthioethanol, and mustard chlorohydrin formed in addition to polysulfides and some uncharacterized compounds (D'Agostino and Provost, 1985, cited in Rosenblatt, et al., 1995). Bulk HD can persist deep in the soil or under quiescent water for years (Rosenblatt, et al., 1995). This persistence is thought to be the result of a layer of oligomeric polysulfide degradation products formed by limited hydrolysis (Rosenblatt, et al., 1995). In one experiment equal volumes of HD and water were allowed to stand. After two months at least 50% of the original HD

phase still was present. NMR data indicated that the most abundant product was the large ion, H-2TG, with lesser amounts of H-TG and CH-TG. There is evidence that these ions could revert back to HD (Yang, et al., 1992). Therefore, alkaline hydrolysis is rarely used to neutralize HD.

Organic solvents have been added to mustard neutralization solutions to solubilize the HD and increase the effective rate of hydrolysis. Often these solvents suppress the formation of the sulfonium ion intermediate, thereby reducing the effective rate of HD hydrolysis. The addition of 5% acetone to HD in water was found to double the half-life of HD in water (Yang, et al., 1986, cited in Rosenblatt, et al., 1995).

Because the sulfur atom in HD can be oxidized, oxidation is an important approach to the neutralization of mustard. Hypochlorite bleaches have been used for this purpose. The reaction depends upon the proportions of reactants and temperature. It is thought to proceed through formation of the sulfoxide and the sulfone of HD followed by a series of elimination reactions (Rosenblatt, et al., 1995). Under optimum conditions (excess chemical neutralization reagent, high pH, and adequate stirring) hypochlorite will oxidize HD to sulfate, chloride and carbon dioxide according to the following equation:

$$(ClCH_2CH_2)_2S + 14\ OCl^- \rightarrow SO4^{-2} + 16\ Cl^- + 4\ CO_2 + 4\ H^+ + 2\ H_2O$$

^{13}C NMR analysis of one such reaction mixture revealed more than 99.5% destruction of HD and the formation of about 20 uncharacterized carbon-containing products. With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of HD may persist (Durst, et al., 1988). Oxidation is favored in basic solutions of hypochlorite and HD. In neutral or acidic solutions chlorination takes place (Rosenblatt, et al., 1995).

Little is known about the effect of hypochlorite upon the impurities produced during the manufacture of H/HD. It is likely that conditions favorable to the complete mineralization of HD to sulfate, chloride and carbon dioxide also will oxidize the additional sulfur atoms in the polysulfides. Other sulfur-containing impurities probably would be oxidized as well, if not to sulfate, at least to sulfoxides, sulfones or sulfonic acids (Rosenblatt, et al., 1995).

2.2.1.11 HT

CAS Reg. No.: Not Available for HT For agent T: 63918-89-8, HT is a 60% / 40% mixture of HD and another blister agent designated as T.

Synonyms for agent T:
Bis-(2-(2-chloroethylthio))ethyl ether
Di (2-(2-chloroethylthio))ethyl ether

Di (2-(B-chloroethyl thio))ethyl ether

Properties:
Agent T is a mustard, but was not used as a separate filling in munitions. It was mixed with HD to lower the melting point of the HD (Operation Plan, 1978).

Table 2.2-13 presents the environmentally relevant properties of HT (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-13. Environmentally Relevant Properties of HT.

Property	Data	Reference
Empirical Formula HD T	$C_4H_8Cl_2S$ $C_8H_{16}Cl_2OS_2$	Field Manual 3-9, 1990
Molecular Weight	HD: 159.08 g/mol T: 263.3 g/mol HT: 189.4 g/mol (Average based on 60:40 weight percent)	Field Manual 3-9, 1990
Liquid Density	1.269 g/cm^3 at 25°C	Field Manual 3-9, 1990
Melting Point	0.0 to 1.3°C (60/40 mixture)	Field Manual 3-9, 1990
Boiling Point	Above 228°C	Field Manual 3-9, 1990
Heat of Vaporization	Not Available	Not Available
Vapor Pressure	0.104 mm Hg at 25°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L)	Barely soluble in water.	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	831 mg/m^3 at 25°C	Field Manual 3-9, 1990

Reactions:
Although T has not been studied as a separate agent, its structure is very close to HD and its chemistry is expected to be very similar to that of HD (Durst, et al., 1988).

2.2.1.12 HQ

CAS Reg. No.: Not Available for HQ. For agent Q: 3563-36-8. HQ is a mixture of HD and another blister agent designated as Q. The usual mixture is 75% HD and 25% Q (Safety Office, 1995).

Synonyms for agent Q:

Sulfur sesquimustard

1,2-bis(2-chloroethylthio)ethane

Doppel-Q

Sesqua yperite

Properties:

Agent Q is used exclusively in a mixture with HD to increase persistence. Q is the most powerful known military vesicant on bare skin, but it has a low vapor pressure and cannot form a vapor threat. Table 2.2-14 presents the environmentally relevant properties of HQ (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-14. Environmentally Relevant Properties of HQ.

Property	Data	Reference
Empirical Formula HD Q	$C_4H_8Cl_2S$ $C_6H_{12}Cl_2S_2$	Field Manual 3-9, 1990 Burck, et.al.,1992
Molecular Weight	HD: 159.08 g/mol Q: 219.13 g/mol	Field Manual 3-9, 1990 Burck, et.al.,1992
Liquid Density Q	1.27 g/cm^3 at 20°C	Burck, et.al.,1992
Melting Point Q	52-54°C	Burck, et.al.,1992
Boiling Point Q	353°C (calculated)	Burck, et.al.,1992
Heat of Vaporization	Not Available	Not Available
Vapor Pressure Q	0.00005 mm Hg at 25°C	Burck, et.al.,1992
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L) Q	Barely soluble in water.	Burck, et.al.,1992
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility Q	0.16 mg/m^3 at 25°C	Burck, et.al.,1992

Reactions:

The structure of agent Q is closely related to that of HD, therefore the reactions of agent Q are expected to be similar to those of HD.

2.2.1.13 L (Lewisite)

CAS Reg. No.: 541-25-3

Synonyms:
(2-Chlorovinyl) dichloroarsine
(2-Chloroethenyl) arsonous dichloride
Chlorovinylarsine dichloride
2-Chlorovinyldichloroarsine
Beta-chlorovinyldichloroarsine
Dichloro (2-chlorovinyl) arsine
EA 1034

Properties:
L is an arsenical vesicant produced for use in World War II. Stored L contains four substances. L-1, 2-chlorovinyldichloroarsine, is the primary component. L-2, bis-(2-chlorovinyl)chloroarsine, also is a vesicant and may be present up to 10% or 20%. Some arsenic trichloride ($AsCl_3$) is present as well (Yurow and Davis, 1982). L-3, tris(2-chlorovinyl)arsine is present as an impurity in stored L. It is not a vesicant (Jackson and Jackson, 1935).

Table 2.2-15 presents the environmentally relevant properties of L (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-15. Environmentally Relevant Properties of L.

Property	Data	Reference
Empirical Formula	$C_2H_2AsCl_3$	Field Manual 3-9, 1990
Molecular Weight	207.35 g/mol	Field Manual 3-9, 1990
Liquid Density	1.89 g/mL at 20°C	Field Manual 3-9, 1990
Melting Point	-18°C	Field Manual 3-9, 1963
Boiling Point	190°C	Field Manual 3-9, 1990
Heat of Vaporization	58 cal/g from 0°C to 190°C	Field Manual 3-9, 1990
Vapor Pressure	0.087 mm Hg at 0°C 0.394 mm Hg at 20°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L)	Insoluble in water.	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{oc}	Not Available	Not Available
Volatility	4.48 x 10^3 mg/m^3 at 20°C	Field Manual 3-9, 1990

Reactions:

When subjected to basic solutions L decomposes to arsenite, chloride, and acetylene according to the following equation:

$$ClCH{=}CHAsCl_2 + 6\ NaOH \rightarrow Na_3AsO_3 + 3\ NaCl + H_2C_2 + 3\ H_2O$$

Yurow and Davis (1992) report this reaction to be complete in less than 10 seconds with a heat of reaction of -102,000 cal/mol. L-2 appears to decompose more slowly in aqueous sodium hydroxide than does L-1. L-2 in chloroform has been neutralized with aqueous sodium hydroxide.

Durst and coworkers (1988) cited a report by Bartlett (1942) that the cis and trans isomers of L react at different rates in 16% sodium hydroxide, but the reaction for both isomers was found to be complete in approximately one hour. C. L. Hewitt (1948) reported that the manufacture of L with an $AlCl_3$ catalyst produces 100% trans-L, while the use of $HgCl_2$ or CuCl catalysts results in a mixture of 90% trans and 10% cis isomers. The cis isomer was the slower of the two to react with base. Hewitt also noted that the cis isomer dissolved in cold NaOH without the evolution of acetylene and formed vinyl chloride when the solution was warmed to 40°C. Smith and coworkers (1993) reported the analysis of a sample of distilled L. They found 95% trans isomer, <2% cis isomer and 3% of a geminal isomer that has the chlorine attached to the carbon atom that is bonded to arsenic. The presence of the geminal isomer may explain the behavior of Hewitt's "cis isomer". Waters and Williams (1950) reported that at 16°C the pH of a solution of L must be at least 10.5 to from acetylene, and that the pH must be at least 9 to form acetylene at 50°C. Because of the relative insolubility of L or its oxide in aqueous solutions, the use of a cosolvent such as an alcohol has been recommended (Durst, et al., 1988).

Durst and coworkers (1988) cited a report by Buswell and Price (1944) that the reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation in solution, it offers no advantage over aqueous sodium hydroxide. According to Durst and coworkers (1988), the reaction of L with hypochlorite in aqueous solution proceeds as an alkaline hydrolysis, producing arsenate, chloride, and acetylene with the hypochlorite serving as a source of hydroxide according to the following equilibrium.

$$OCl^- + H_2O \leftrightarrow HOCl + OH^-$$

One reference noted that L reacts with dry STB with the liberation of chlorine (Davis, et al., 1979). Another report described a three-step process for the chemical neutralization of L. It consisted of conversion of L to Lewisite oxide by addition of the agent to aqueous caustic hydrogen peroxide under controlled pH conditions, followed by removal of excess peroxide, and then conversion of the Lewisite oxide to arsenate and chloride salts. No details were given (Mcandless and Fedor, 1992).

L in H_2O reacts rapidly to give lumps that are soluble only upon prolonged stirring and are polymeric modifications of Lewisite oxide, ClCH=CHAsO. The aqueous solution of Lewisite oxide has vesicant properties (Durst, et al., 1988). The degree of polymerization of the residue depends upon age. Oxidation of Lewisite oxide to the pentavalent state markedly reduces its toxicity (Yurow and Davis, 1982).

2.2.1.14 HL

CAS Reg. No.: Not Available

Synonyms:
Sulfur Mustard/Lewisite

Properties:
HL is a variable combination of HD and L that provides a mixture of low freezing point for use in cold weather operations or high-altitude spray. Table 2.2-16 presents the environmentally relevant properties for the eutectic mixture (37% HD / 63% L by weight), which has the lowest possible freezing point (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-16 Environmentally Relevant Properties of HL.

Property	Data	Reference
Empirical Formula HD: L:	$C_4H_8Cl_2S$ $C_2H_2AsCl_3$	Field Manual 3-9, 1990
Molecular Weight Eutectic Mixture (37% HD/63%L)	HD: 159.08 g/mol L: 207.35 g/mol "186.4 g/mol"	Field Manual 3-9, 1990
Liquid Density	Approx. 1.66 g/mL at 20°C	Field Manual 3-9, 1990
Melting Point purified agent mix: typical production batch:	 -25.4°C -42°C	Material Safety Data Sheet for HL
Boiling Point	Indefinite, but below 190°C	Field Manual 3-9, 1990
Heat of Vaporization	Between HD & L	Field Manual 3-9, 1990
Vapor Pressure	0.248 mm Hg at 20°C (Calculated)	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L)	Practically insoluble.	Material Safety Data Sheet for HL
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	2,730 mg/m^3 at 20°C (Calculated)	Field Manual 3-9, 1990

Reactions:
The chemical neutralization of HL is expected to proceed as parallel neutralizations of HD and L with a mixture of neutralization products from the two processes.

2.2.1.15 HN-1

CAS Reg. No.: 538-07-8
Synonyms:
Bis(2-chloroethyl)ethylamine
Ethylbis (2-chloroethyl)amine
Nitrogen Mustard (HN-1)
Ethyl S
NH-Lost

Properties:
HN-1 is a vesicant similar to HD in its properties and effects, but only one-fifth as damaging and not as stable. It is more volatile, and therefore less persistent, than HD (Field Manual 3-9, 1990).

Table 2.2-17 presents the environmentally relevant properties of HN-1 (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-17. Environmentally Relevant Properties of HN-1.

Property	Data	Reference
Empirical Formula	$C_6H_{13}Cl_2N$	Field Manual 3-9, 1990
Molecular Weight	170.08 g/mol	Field Manual 3-9, 1990
Liquid Density	1.09 g/mL at 25°C	Field Manual 3-9, 1990
Melting Point	-34°C	Field Manual 3-9, 1990
Boiling Point	194°C (Calculated; decomposes)	Field Manual 3-9, 1990
Heat of Vaporization	77 cal/g	Field Manual 3-9, 1990
Vapor Pressure	0.24 mm Hg at 25°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L)	Sparingly soluble in water.	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	308 mg/m^3 at 0°C 1,520 mg/m^3 at 20°C	Field Manual 3-9, 1990

Reactions:
The nitrogen mustards hydrolyze in water to give products related to the formation of an aziridinium (or ethyleneimmonium) ion. Therefore, basic solutions are preferred for chemical neutralization. The

hydrolysis half-life of HN-1 in dilute sodium hydroxide was described as being 12 minutes at 18° C, but the overall neutralization rate was limited by the low solubility of HN-1. Some neutralization work has been reported using monoethanolamine. The only information found concerning aqueous oxidative neutralization of the nitrogen mustards was a reference to some exploratory studies (Yurow and Davis, 1982).

2.2.1.16 HN-3

CAS Reg. No.: 555-77-1

Synonyms:
Tris(2-chloroethyl)amine
2,2′,2′′-Trichlorotriethylamine
Tri(2-chloroethyl)amine
Nitrogen Mustard (HN-3)

Properties:
HN-3 is the principal representative of the nitrogen mustards because it has vesicant properties almost equal to those of HD. It is more persistent than HD. It also is the most stable in storage of the three nitrogen mustards. (Field Manual 3-9, 1990). Table 2.2-18 presents the environmentally relevant properties of HN-3 (Field Manual 3-9, 1990). The quality of the data presented in this table has not been evaluated.

Table 2.2-18. Environmentally Relevant Properties of HN-3.

Property	Data	Reference
Empirical Formula	$C_6H_{12}Cl_3N$	Field Manual 3-9, 1990
Molecular Weight	204.54 g/mol	Field Manual 3-9, 1990
Liquid Density	1.24 g/mL at 25°C	Field Manual 3-9, 1990
Melting Point	-3.7°C	Field Manual 3-9, 1990
Boiling Point	256°C (Calculated; decomposes)	Field Manual 3-9, 1990
Heat of Vaporization	74 cal/g	Field Manual 3-9, 1990
Vapor Pressure	0.0109 mm Hg at 25°C	Field Manual 3-9, 1990
Log K_{ow}	Not Available	Not Available
Aqueous Solubility (g/L)	Insoluble in water.	Field Manual 3-9, 1990
K_H (atm-m^3/mol)	Not Available	Not Available
Diffusion Coefficient (air) (cm^2/s)	Not Available	Not Available
Log K_{OC}	Not Available	Not Available
Volatility	13 mg/m^3 at 0°C 121 mg/m^3 at 25°C 180 mg/m^3 at 30°C	Field Manual 3-9, 1990

Reactions:

The reactions of HN-3 are expected to be similar to the reactions of HN-1.

2.2.2 Chemical Neutralization Solutions

This section discusses neutralization solutions in the following sections.

- Chemical Neutralization Solutions Used at DPG
- Chemical Neutralization Solution Reactions
- Spent Chemical Neutralization Solutions

2.2.2.1 Chemical Neutralization Solutions Used at DPG

There are seven chemical neutralization solutions routinely used at DPG. They fall into two categories: chlorinated bleaches and caustics. The neutralization solutions for chemical agents are listed in Table 2.2-19. The contact times listed are the minimum times recommended for the reaction of the chemical agent with the listed neutralization solution before sampling to verify complete neutralization.

Table 2.2-19. Selection of Chemical Neutralization Solutions.

Neutralization Solution	GA, GB, GF, Vx	GD	H, HD, HT, HNs	L, HL	VX
10% aqueous HTH	15 min	15 min	15 min	15 min	15 min
STB Slurry (aqueous)	15 min	15 min	15 min	15 min	15 min
5% aqueous NaOCl	24 hr	24 hr	24 hr	24 hr	24 hr
Concentrated NH_4OH	4 hr NR for Vx	4 hr	NR	NR	NR
10% aqueous Na_2CO_3	4 hr	NR	NR	NR	NR
10% aqueous NaOH	4 hr	NR	NR	NR	4 hr
10% NaOH in alcohol (a)	24 hr	24 hr	NR	NR	24 hr

NR Not Recommended

2.2.2.2 Chemical Neutralization Solution Reactions

According to Durst and coworkers (1988), the term "hydrolysis" refers to the addition of water to a reactive molecule with the elimination of some fragment of the reactive molecule into the aqueous solution. For example, water will react with GB according to the following equation:

$$GB + H_2O \rightarrow IMPA + HF$$

The concept of hydrolysis includes the reactions of the ions of water, which are OH^- and H^+. These are referred to as alkaline and acid hydrolysis, respectively. If OH^- is added to a solution containing GB, the alkaline hydrolysis reaction is very rapid. In the case of GB the anion of IMPA and fluoride ion are formed. The reaction of GB with water is too slow to be practical as a neutralization procedure. However, the reaction of GB with hydroxide ion is a very effective approach to the neutralization of that

chemical agent. More OH^- is consumed in the alkaline hydrolysis of GB because additional hydroxide is used to neutralize the acid products formed. The equation for the alkaline hydrolysis of GB is written as follows:

$$GB + 2\,NaOH \rightarrow Na[IMPA] + NaF + H_2O$$

where: Na[IMPA] is the sodium salt of IMPA

GB will undergo alkaline hydrolysis in the same way without regard to the source of OH^-. Thus, GB will hydrolyze to produce the same organic anion product, IMPA, when reacted with NaOH, Na_2CO_3, or NH_4OH because all are sources of hydroxide ion in aqueous solution. For example, Na_2CO_3 forms hydroxide in aqueous solution according to the following equation:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$$

Different sources of OH^- are employed because in many deliberate chemical neutralization situations military units have a need to reuse the neutralized item. NaOH corrodes equipment made of aluminum and magnesium. Therefore, Na_2CO_3 often is used to neutralize reusable items made from such materials because it does not corrode them. NH_4OH also is a weaker source of hydroxide ion than NaOH because it is only partially ionized to ammonium and hydroxide ions. Table 2.2-20 lists approximate pH values for various concentrations of bases used for alkaline hydrolysis of chemical agents – the higher the pH, the higher the hydroxide concentration (Durst, et al., 1988).

Table 2.2-20. Approximate pH Values of Solutions of Various Concentrations of Selected Bases.

Selected Baset	pH in 0.1 N Base	pH in 0.01 N Base
NaOH	13.1	12.1
Na_2CO_3	11.5	11.0
NH_4OH	11.3	10.8

NaOH is comparatively inexpensive and offers the highest pH at a particular concentration, therefore in the absence of other considerations it often is chosen as the source of hydroxide ion for chemical agent waste neutralization by alkaline hydrolysis at DPG. Informal interviews with members of the DPG laboratory staff on February 24, 1998 found that NaOH and alcoholic NaOH usually were used routinely for chemical neutralization by alkaline hydrolysis in the CCTF.

The chemical agents undergo the same oxidation reactions with hypochlorite ion whether the hypochlorite ion comes from NaOCl, STB, or HTH. The use of hypochlorite in neutralization of mustard and VX depends upon the oxidative action of hypochlorite upon sulfur in mustard and upon nitrogen and sulfur in VX. When more than a small quantity of agent is oxidized, the reaction is vigorous and care must be taken to control the rate at which heat is produced. A lower concentration of neutralization

solution may be used or the rate of addition of agent to the neutralization solution may be controlled to moderate the oxidation reaction.

Apart from its oxidative capability, hypochlorite also can function as a nucleophile, hydrolyzing G-agents in a way similar to the hydroxide ion. The normal hydroxide ion hydrolysis products from the G-agents also are produced by hypochlorite ion. In the case of GA the dimethylamino group is lost in addition to the cyano group (Durst, et al., 1988).

2.2.2.3 Spent Chemical Neutralization Solutions

Although a number of different neutralization solutions are used for chemical neutralization, the reactions that achieve neutralization of the chemical agents used in testing at DPG fall into two categories: hydrolysis or oxidation. The concentration but not the chemical source of the hydroxide or hypochlorite ions determines the reaction pathways and the rates of the neutralization reactions with the chemical agents. A variety of compounds remain in the neutralization solutions after use.

Hypochlorite solutions that have stood for any length of time contain chlorate ion as a contaminant because of the disproportionation equilibrium shown by the following equation (Bodek, et al., 1988, cited in Rosenblatt, et al., 1998).

$$2\ HOCl + OCl^- \leftrightarrow ClO_3^- + 2\ Cl^- + 2\ H^+$$

Chlorate ion should not be overlooked as a possible contaminant.

Fluoride ion results from the neutralization of GB, GD, and GF. Alkyl methylphosphonic acids result from the neutralization of the G-agents and VX. Thiodiglycol is the product of the complete hydrolysis of mustard. The alkaline chlorinolysis of VX produces alkyl phosphonic acid and diisopropylamine. Tributylamine, sometimes added to GB, is unaffected by hydrolysis. It probably would be oxidized to dibuytylamine and butyraldehyde by hypochlorite (Rosenblatt, et al., 1995). Cyanide ion is formed when GA is neutralized using aqueous hydroxide. It may be necessary to treat the solution with hypochlorite to convert the cyanide to nitrogen gas and carbonate ion (Yurow, 1988). Solutions resulting from the hydrolysis of L contain arsenite ion (AsO_3^{-3}) or arsenate ion ($AsO_4)^{-3}$.

The stabilizers, N,N′-diisopropylcarbodiimide and N,N′-dicyclohexylcarbodiimide, are hydrolyzed to the respective ureas. Under conditions of chlorinolysis the ureas could become N,N′-dichlorinated.

Under some circumstances organic solvents (alcohol, acetone) remain after being added to solubilize agents such as thickened GD, HD, or VX. In other situations solutions of chemical agents in solvents

such as chloroform or carbon tetrachloride are neutralized and the residual solvents become part of the waste stream.

Under dehydrating conditions the alkyl methyl phosphonates from the hydrolysis of G-agents and VX can form anhydrides. This is not expected to occur in aqueous solutions. It is highly unlikely that VX, once hydrolyzed, would reform under any conditions. One of the major hydrolysis products of VX, diisopropylaminoethanethiol, can be air oxidized to a reputedly vesicant disulfide (Rosenblatt, et al., 1995).

3.0 SUPPORT FOR CHEMICAL NEUTRALIZATION OF CHEMICAL AGENT WASTE STREAMS AS APPLICABLE AND DEMONSTRATED TREATMENT TECHNOLOGIES

The purpose of this section is to provide support of the chemical neutralization of the DPG chemical agent-related waste streams as technologies that are applicable LDR treatment technologies based on data from DPG to evaluate whether the technologies are demonstrated.

To be considered applicable, a technology must theoretically be capable of treating either the waste in question or a waste that is similar in terms of the parameters that affect the selection of the treatment methods. Parameters that affect treatment performance may include physical and chemical characteristics, such as pH, bond disassociation energy, thermal conductivity, inorganic and organic composition and concentration of the constituents of concern..

To be considered demonstrated, a technology must be employed in operation for the treatment of the waste in question or a similar waste. Technologies may also be considered for other wastes with similar parameters (such as physical and chemical characteristics) that affect treatment performance.

To support the neutralization of chemical agent-related waste streams as applicable and demonstrated treatment technologies, this section presents the following topics:

- The applicability of chemical neutralization as a treatment technology
- The performance database

3.1 APPLICABILITY OF CHEMICAL NEUTRALIZATION AS A TREATMENT TECHNOLOGY

Chemical neutralization procedures used at DPG are evaluated as applicable using the following categories: general chemistry, NMR data, thermodynamics and kinetics of the reaction, and the re-formation of chemical agent from neutralization products. The chemical reactions involved in the neutralization procedures used at DPG have been studied extensively and a large amount of data have been gathered. General chemistry is described in Section 2.0. A description of the other categories follow.

NMR evidence is significant because it provides unambiguous information regarding disappearance of the chemical agent and appearance of the neutralization products in the same reaction mixture at the same time. It also provides information on how "clean" a neutralization reaction is, that is, the number of side products and their approximate concentrations. The NMR measurements reviewed in this report have a detection limit of approximately 0.5%. Therefore, components present at less than 0.5% do not appear in the NMR spectra referenced in this discussion (Durst, et al., 1988).

The equilibrium constant for a reaction (K_{eq}) can be calculated from the change in free energy of the reaction according to the relationship:

$$\Delta G = -2.303\ RT \log K_{eq}$$

where: ΔG is the change in free energy ($G_{products} - G_{reactants}$)
R is the gas constant, and
T is the absolute temperature.

A large negative change in free energy corresponds to an equilibrium constant that favors the products of the reaction. The free energy of a reaction is related to the heat of reaction by the equation:

$$\Delta G = \Delta H - T\Delta S$$

where: ΔH is the heat of reaction, or change in enthalpy ($H_{products} - H_{reactants}$)
T is the absolute temperature, and
ΔS is the change in entropy ($S_{products} - S_{reactants}$)

If the products and reactants both remain in solution the entropy term, $T\Delta S$, usually does not change a large amount. This leads to the general observation that an exothermic reaction which has a large negative ΔH will have a negative ΔG term, indicating an equilibrium favoring the products.

The chemical agent neutralization reactions are exothermic, and in some instances very exothermic. Using the equations given above and tables of thermodynamic values, it is possible to estimate the free energies of reactions and their corresponding equilibrium constants. This has been done for the alkaline hydrolysis of GB in the following equation:

$$GB + OH^- \rightarrow \text{IMPA anion} + F^-$$

The ΔH = -44,400 cal/mol (Davis, et al., 1977). The ΔG has been calculated to be -30,000 cal/mol, and the resulting equilibrium constant is estimated at log K_{eq} = 21.9, indicating a very strong tendency to favor completion of the reaction (Durst, et al., 1988).

Free energy of a reaction must be negative in order for the reaction to proceed. However, a negative free energy does not guarantee that a reaction will proceed. Non-thermodynamic factors also significantly affect reaction rates. Thermodynamic predictions must be evaluated in light of measured reaction rate data. Generally, the chemical agent neutralization reactions are exothermic and generally the recommended neutralization reactions proceed rapidly in solution. The principal non-thermodynamic

factor that requires consideration in neutralization processes is agent solubility in water. HD and VX, for example, are less than 1% soluble in water at room temperature (Field Manual 3-9, 1990). The thermodynamics and kinetics of each agent/neutralization reaction are discussed. Table 3.1-1 presents heats of reaction and half-lives for chemical reactions resulting from the neutralization procedures at DPG.

Table 3.1-1. Thermochemical and Kinetic Data.

Chemical Agent	Neutralization Solution	Heat of Reaction	Half Life	Reference
GA	Water, pH 9.5	Not Available	35 min/25° C	Yurow and Davis (1982)
GA	Aqueous OH^- pH 12	Not Available	9.2 sec	Durst, et al (1988)
GA	Sodium hydroxide	-10.1 kcal/mol	Not Available	Yurow and Davis (1982)
GB	Sodium hydroxide	-44.4 kcal/mol	Not Available	Yurow and Davis (1982)
GB	5% Sodium hydroxide	Not Available	< 0.8 sec/25° C	Yurow and Davis (1982)
GB	10% Sodium carbonate	-22 kcal/mol	8.5 sec/25° C	Yurow and Davis (1982)
GB	Water, pH 10	Not Available	~ 4 min/25° C	Yurow and Davis (1982)
GB	Water, pH 10	Not Available	5 min/25° C	Demek, et al. 1970, cited in Rosenblatt, et al. (1995)
GB	5% Alkaline bleach	Not Available	Instantaneous/25° C	Yurow and Davis (1982)
GD	5% Sodium hydroxide	Not Available	0.08 hr/20° C	Yurow (1988)
VX	Alkaline hypochlorite	Approx. –700 kcal/mol	Not Available	Yurow and Davis (1982)
VX	10% HTH slurry	Not Available	~ 70 sec/25° C	Yurow and Davis (1982)
VX	Water, pH 14	Not Available	1.3 min/25° C	Yurow and Davis (1982)
VX	Water, pH 12	Not Available	2.5 hr/25° C	Epstein, et al. 1974, cited in Rosenblatt, et al., 1995
HD	Alkaline hypochlorite	Highly exothermic	Not Available	Yurow and Davis (1982)
L	Sodium hydroxide	-102 kcal/mol	Not Available	Yurow and Davis (1982)
L	5% Sodium hydroxide	Not Available	Instantaneous/25° C	Yurow and Davis (1982)
L	Water	Not Available	Very fast/25° C	Yurow and Davis (1982)
HN-1	Dil. Sodium hydroxide	Not Available	12 min/18° C	Yurow and Davis (1982)

In general, there is not evidence to support re-forming agent in dilute, unmodified chemical neutralization solutions. When the products of neutralization are concentrated or modified there is a possibility that some agents could re-form.

The principal chemical reaction(s) for each agent/neutralization solution pair used at DPG is described in the following sections. The presence of impurities and additives will be identified and their reactions will be discussed.

3.1.1 Chemical Neutralization of GB by Alkaline Hydrolysis

GB is miscible with water (Field Manual 3-9, 1990). DPG routinely neutralizes GB with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na_2CO_3, and concentrated NH_4OH. This discussion applies specifically to the chemical neutralization of GB in 10% aqueous NaOH. It applies generally to the following three additional procedures: GB in 10% NaOH in alcohol, GB in 10% aqueous Na_2CO_3, and GB in concentrated NH_4OH.

The neutralization of GB in sodium hydroxide proceeds by the following reaction:

$$GB + 2\,NaOH \rightarrow Na[IMPA] + NaF + H_2O$$

where: Na[IMPA] is the sodium salt of IMPA
NaF is sodium fluoride

The ^{31}P NMR evidence indicates that greater than 99.5% GB proceeds to greater than 99.5% Na[IMPA] with phosphorus containing side products less than 0.5%. Similar NMR results have been reported for the neutralization of GB in 10% NaOH in alcohol, and the neutralization of GB in 10% aqueous Na_2CO_3 (Durst, et al., 1988). Table 3.1-2 presents the starting materials and final products in the alkaline hydrolysis of GB (Rosenblatt, et al., 1995).

Table 3.1-2. Products of Alkaline Hydrolysis of GB.

Principal Starting Materials	Principal Final Products
GB	Na[IMPA] NaF
Trace Starting Materials	**Trace Final Products**
Methylphosphonic difluoride	MPA
	F^- (Fluoride ion)
Diisopropyl methylphosphonate (DIMP)	DIMP (Hydrolyzes slowly to IMPA)
N,N'-Diisopropylcarbodiimide	N,N'-Diisopropyl urea
Tributylamine	Tributylamine

The ΔH for the alkaline hydrolysis of GB is –44,400 cal/mol (Davis, et al., 1977). An equilibrium constant of $10^{21\,9}$ has been calculated from a ΔG of -30,000 cal/mol (Durst, et al., 1988). GB is infinitely soluble in water. At 25°C and at pH 10 the half-life of GB is 5 minutes (Demek, et al., 1970, cited in Rosenblatt, et al., 1995). Yurow and Davis (1982) give a half-life of ~ 4 minutes for GB under the same conditions. They also report a half-life of <0.8 seconds for GB in 5% sodium hydroxide.

The term "toxic rebound" has been used to describe the re-formation of a small amount of GB when brine containing the hydrolyzed salts from alkaline hydrolysis of GB is spray dried. The more concentrated the salt solutions and the higher the acidity of the solution being spray dried, the higher the

yield of GB will be. This re-formation phenomenon is of concern only when concentrations of the participating chemical species are high and heat is applied (Rosenblatt, et al., 1995).

Beaudry and coworkers (1993) investigated the possibility of G-agents re-forming in a 300-gallon neutralization tank that had been used for a series of neutralization reactions. The G-agents observed in that investigation finally were attributed to GB forming in the chloroform extract of acidified samples of the neutralization solution. Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt, et al., 1995).

3.1.2 Chemical Neutralization of GB with Hypochlorite

DPG routinely neutralizes GB with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GB in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the neutralization of GB is to provide hydroxide ion and to accelerate the reaction (Yurow, 1982).

The chemical neutralization of GB in hypochlorite is an alkaline hydrolysis, with hypochlorite serving to accelerate the reaction. The reaction is described by the same equation that is used for alkaline hydrolysis:

$$GB + 2\ NaOH \rightarrow Na[IMPA] + NaF + H_2O$$

The ^{31}P NMR evidence indicates that greater than 99.5% GB proceeds to greater than 99.5% Na[IMPA] in 5.25% NaOCl with phosphorus containing side products less than 0.5% (Durst, et al., 1988). Table 3.1-3 summarizes the starting materials and final products in the alkaline hydrolysis of GB in hypochlorite solution (Rosenblatt, et al., 1995).

Table 3.1-3. Products of Alkaline Hydrolysis of GB in Sodium Hypochlorite Solution.

Principal Starting Materials	Principal Final Products
GB	Na[IMPA] NaF
Trace Starting Materials	**Trace Final Products**
Methylphosphonic difluoride	MPA F^- (Fluoride ion)
DIMP	DIMP slowly hydrolyzes to IMPA
N,N′-Diisopropylcarbodiimide	N,N′-Diisopropyl urea (Possible reversible N,N′-chlorination of the urea, if hypochlorite is in high enough concentration.)
Tributylamine	Probably dibutylamine + butyraldehyde
Hypochlorite (OCl^-)	Chlorate (ClO_3^-)

The reaction is exothermic, but a value for the heat of reaction is not available. The reaction rate has been reported as "instantaneous" (Yurow and Davis, 1982).

Based on the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GB from the products resulting from reaction with hypochlorite is not expected.

3.1.3 Chemical Neutralization of GA by Alkaline Hydrolysis

GA has a solubility in water of 7.2% at 20° C (Field Manual 3-9, 1990). DPG routinely neutralizes GA with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na_2CO_3, and concentrated NH_4OH. This discussion applies specifically to the chemical neutralization of GA in 10% aqueous NaOH. It applies generally to three additional procedures: GA in 10% NaOH in alcohol, GA in 10% aqueous Na_2CO_3, and GA in concentrated NH_4OH.

The neutralization of GA in 10% aqueous sodium hydroxide proceeds by the following reaction:

$$GA + 2\ NaOH \rightarrow Na[\text{ethyl dimethylaminophosphonate}] + NaCN + H_2O$$

where: Na[ethyl dimethylaminophosphonate] is the sodium salt of ethyl dimethylaminophosphonic acid

When sufficient quantities of GA are neutralized using aqueous hydroxide, it becomes necessary to destroy the cyanide ion that is produced to prevent formation of HCN if the solution is acidified. After neutralization is complete treating the solution with hypochlorite will convert the cyanide to nitrogen gas and carbonate ion (Yurow, 1988).

The ^{31}P NMR evidence indicates that greater than 99.5% GA procceds to greater than 99.5% Na[ethyl dimethylaminophosphonate] with phosphorus containing side products less than 0.5%. Similar NMR results have been reported for the neutralization of GA in 10% NaOH in alcohol, and the neutralization of GA in 10% aqueous Na_2CO_3 (Durst, et al., 1988). Table 3.1-4 (Yurow, 1988; Rosenblatt, et al., 1995) presents the starting materials and final products in the alkaline hydrolysis of GA.

Table 3.1-4. Products of Hydrolysis of GA in Sodium Hydroxide.

Principal Starting Materials	Principal Final Products
GA	Na[ethyl dimethylaminophosphonate], the sodium salt of ethyl dimethylaminophosphonic acid NaCN (sodium cyanide)
Trace Starting Materials	**Trace Final Products**
DIMP	DIMP very slowly hydrolyzes to IMPA

The ΔH for the alkaline hydrolysis of GA at pH 9.5 and 25° C has been reported as −10,100 cal/mol. The half-life for that reaction was reported as 35 minutes (Yurow, 1988). The half-life for the same reaction at pH 12 was reported to be 9.2 seconds (Durst, et al., 1988).

Based on the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GA from its alkaline hydrolysis products is not expected.

3.1.4 Chemical Neutralization of GA with Hypochlorite

DPG routinely neutralizes GA with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GA in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the neutralization of GA is to provide hydroxide ion and to accelerate the reaction.

According to Durst and coworkers (1988), when GA is neutralized with hypochlorite both the cyano group and the dimethylamino group are lost, producing the ethyl ester of phosphonic acid. The other products of the reaction were not identified. The hypochlorite will react with the cyanide, converting it to nitrogen gas and carbonate ion (Yurow, 1988).

The ^{31}P NMR evidence indicates that greater than 99.5% GA proceeds to greater than 99.5% Na[ethyl phosphonate] with phosphorus containing side products less than 0.5%. Table 3.1-5 (Yurow, 1998; Durst, et al., 1988; Rosenblatt, et al., 1995) presents the starting materials and final products in the alkaline hydrolysis of GA.

Table 3.1-5. Reaction of GA with Sodium Hypochlorite.

Principal Starting Materials	Principal Final Products
GA	Na[ethyl phosphonate], the sodium salt of ethyl phosphonic acid Possibly dimethylamine
Trace Starting Materials	**Trace Final Products**
DIMP	DIMP slowly hydrolyzes to IMPA
OCl^-	Chlorate (ClO_3^-)

The heat of reaction for the neutralization of GA with hypochlorite has not been reported. It is expected to be exothermic by comparison with the alkaline hydrolysis of GA. Hypochlorite has been reported to catalyze the alkaline hydrolysis of GB, and is expected to play a similar role in the reaction with GA (Yurow, 1982).

Because the cyanide is converted irreversibly to nitrogen gas and carbonate ion, no re-formation of GA is expected after chemical neutralization with hypochlorite.

3.1.5 Chemical Neutralization of GD by Alkaline Hydrolysis

GD has a solubility of 2.1% in water at 20° C (Field Manual 3-9, 1990). Like the other G-agents, it is susceptible to alkaline hydrolysis. Because of the low solubility of GD in water, addition of an alcohol can increase solubility and therefore the overall rate of neutralization (Rosenblatt, et al., 1995). DPG routinely neutralizes GD with 10% NaOH in alcohol (10% NaOH in a mixture of 80/20 denatured ethanol and water) and with concentrated NH_4OH. This discussion applies specifically to the chemical neutralization of GD in 10% NaOH in alcohol and generally to the neutralization of GD in concentrated NH_4OH.

The neutralization of GD in alcoholic sodium hydroxide proceeds by the following reaction:

$$GD + 2\ NaOH \rightarrow NaPMPA + NaF + H_2O$$

where: Na[PMPA] is the sodium salt of pinacolyl methylphosphonic acid

The ^{31}P NMR evidence indicates that greater than 99.5% GD proceeds to greater than 99.5% Na[PMPA] with phosphorus containing side products less than 0.5% for the neutralization of GD in 10% NaOH in alcohol. Similar results were found for the neutralization of GD in 10% aqueous NaOH and in 10% aqueous Na_2CO_3 (Durst, et al., 1988).

The presence of alcohol in solution does not significantly inhibit the reactivity of GD or the other G-agents with hydroxide ion. A solution of hydroxide in methanol forms methoxide ion. The methoxide ion reacts as a nucleophile to attack the central phosphorus atom to form the ester, methyl pinacolyl methylphosphonate. This ester eventually undergoes hydrolysis to form PMPA and perhaps some methyl methylphosphonic acid (Rosenblatt, et al., 1995). A set of parallel reactions may occur with GD in ethanol solution. Table 3.1-6 presents the starting materials and final products in the alkaline hydrolysis of GD (Durst, et al., 1988; Rosenblatt, et al., 1995).

Table 3.1-6. Products of Alkaline Hydrolysis of GD.

Principal Starting Materials	Principal Final Products
GD	Na[PMPA] NaF (sodium fluoride)
Trace Starting Materials	**Trace Final Products**
Methylphosphonic difluoride	MPA F^-
DIMP	DIMP slowly hydrolyzes to IMPA
Possible side reaction with ethoxide ion	Possibly ethyl pinacolyl methylphosphonate hydrolyzing to Na[pinacolyl methylphosphonate] and Na[ethyl methylphosphonate]

The half-life of GD in excess 5% aqueous sodium hydroxide is 0.08 hr at 20° C. The heat of reaction is estimated to be similar to that of GB (-44,400 cal/mole) because fluorine is the leaving group in both cases (Yurow, 1988).

Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt, et al., 1995). Re-formation of GD is not expected under the same conditions because of their similar structures and reaction mechanisms.

3.1.6 Chemical Neutralization of GD with Hypochlorite

The DPG routinely neutralizes GD with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GD in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the neutralization of GD is to provide hydroxide ion and to accelerate the reaction (Yurow, 1988).

The neutralization of GD in hypochlorite is an alkaline hydrolysis, with hypochlorite serving to accelerate the reaction. The reaction is described by the same equation that is used for alkaline hydrolysis:

$$GD + 2\ NaOH \rightarrow Na[PMPA] + NaF + H_2O$$

The ^{31}P NMR evidence indicates that greater than 99.5% GD proceeds to greater than 99.5% Na[PMPA] with phosphorus containing side products less than 0.5% for the neutralization of GD in 5.25% NaOCl (Durst, et al., 1988). Table 3.1-7 (Durst, et al., 1988, Rosenblatt, et al., 1995) presents the starting materials and final products in the alkaline hydrolysis of GB in 5.25% NaOCl solution.

Table 3.1-7. Products of Alkaline Hydrolysis of GD in Sodium Hypochlorite Solution.

Principal Starting Materials	Principal Final Products
GD	Na[PMPA] (sodium salt PMPA) NaF
Trace Starting Materials	**Trace Final Products**
Methylphosphonic difluoride	MPA F^-
DIMP	DIMP slowly hydrolyzes to IMPA
OCl^-	ClO_3^-

The reaction is expected to be exothermic. The use of an alcohol in the neutralization solution is expected to increase the overall rate of neutralization by enhancing the solubility. By comparison with GB, the reaction rate is expected to be faster than that of the corresponding alkaline hydrolysis reaction in the same solvent because of the catalytic effect of hypochlorite ion upon alkaline hydrolysis.

Based on the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GD from the products resulting from reaction with hypochlorite solution is not expected.

3.1.7 Chemical Neutralization of TGD

TGD is GD thickened with a polymer. Little specific information was found regarding the neutralization of TGD (thickened GD) or other thickened agents. UCON 75-H-90,000 is a polyethylene glycol derivative that has been used to thicken GB, a related G-agent (Angelotti, et al., 1955). Thickeners are added to GD to increase persistence in the field. In general, thickened agents form large droplets that provide a greater concentration reaching the ground and a greater contact hazard than the unthickened forms (Field Manual 3-9, 1990).

Yang and coworkers (1992) have noted that an organic solvent often is added to an aqueous neutralization solution to improve solubility of thickened agents. The actual neutralization reaction remains the same for the thickened agent after it is in solution. However, many of the oxidation and substitution reactions become slower as the solvent polarity decreases.

The chemical neutralization solution recommended for TGD is 10% NaOH in alcohol.

3.1.8 Chemical Neutralization of GF by Alkaline Hydrolysis

GF is the least soluble of the G-agents considered in this report. It has a solubility of 0.37% in water at 20° C (Field Manual 3-9, 1990). Like the other G-agents, it is subject to alkaline hydrolysis. DPG routinely neutralizes GF with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na_2CO_3, and concentrated NH_4OH.

Little information concerning the alkaline hydrolysis GF was found. Based upon similarities in structure to GB and GD, it is expected to hydrolyze rapidly in alkaline solution according to the reaction:

$$GF + 2\ NaOH \rightarrow Na[\text{cyclohexyl methylphosphonate}] + NaF + H_2O$$

where: Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid

The relative insolubility of GF is expected to lower the overall rate of neutralization. The solution of 10% NaOH in alcohol is expected to be the most effective of the neutralization solutions recommended for use at DPG. Table 3.1-8 presents the starting materials and final products in the alkaline hydrolysis of GF based upon comparison with GB and GD.

Table 3.1-8. Products of Alkaline Hydrolysis of GF.

Principal Starting Materials	Principal Final Products
GF	Na[cyclohexyl methylphosphonate] (sodium salt of cyclohexyl methylphosphonic acid) NaF
Trace Starting Materials	**Trace Final Products**
DIMP	DIMP slowly hydrolyzes to IMPA

By comparison to GB and GD, the reaction is expected to be exothermic and at pH 12 its half-life is expected to be in the range of the half-lives of GB (3 seconds) and GD (7 seconds). It may be necessary to use alcohol to dissolve GF into the neutralization solution.

Re-formation of GB is not expected in dilute aqueous solution at high pH (Rosenblatt, et al., 1995). Similarly, re-formation of GF is not expected under the same conditions because of their similar structures and reaction mechanisms.

3.1.9 Chemical Neutralization of GF with Hypochlorite

DPG routinely neutralizes GF with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of GF in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB. The role of hypochlorite ion in the neutralization of GF is to provide hydroxide ion and to accelerate the reaction (Yurow, 1988).

Little information concerning the reaction of GF with hypochlorite was found. Based upon similarities in structure to GB and GD, it is expected to undergo rapid hydrolysis with hypochlorite serving to accelerate the reaction. The reaction would be described by the same equation that is used for alkaline hydrolysis:

$$GF + 2\ NaOH \rightarrow Na[cyclohexyl\ methylphosphonate] + NaF + H_2O$$

where: Na[cyclohexyl methylphosphonate] is the sodium salt of cyclohexyl methylphosphonic acid

Table 3.19 presents the starting materials and final products expected for the alkaline hydrolysis of GF in 5.25% NaOCl solution based upon comparison with GB and GD.

Table 3.1-9. Products of Alkaline Hydrolysis of GF in Sodium Hypochlorite Solution.

Principal Starting Materials	Principal Final Products
GF	Na[cyclohexyl methylphosphonate] (sodium salt of cyclohexyl methylphosphonic acid) NaF
Trace Starting Materials	**Trace Final Products**
DIMP	DIMP slowly hydrolyzes to IMPA
OCl^-	ClO_3^-

The reaction is expected to be exothermic. The reaction rate is expected to be similar to that of the alkaline hydrolysis reaction, recognizing the effect of limited solubility and the catalytic effect of hypochlorite ion upon alkaline hydrolysis.

Based on the discussion of the possibility of re-formation of GB from its alkaline hydrolysis products, the re-formation of GF from the products resulting from reaction with hypochlorite solution is not expected.

3.1.10 Chemical Neutralization of VX by Alkaline Hydrolysis

VX is only slightly soluble in water at room temperature. Below 9.4°C it is miscible with water. (Field Manual 3-9, 1990). DPG routinely neutralizes VX with 10% aqueous NaOH and 10% NaOH in alcohol.

The hydrolysis of VX proceeds by multiple pathways and results in a more complex set of products than the hydrolysis of the G-agents. Across the pH range the P–S bond is cleaved to give two primary products: EMPA and DESH. EA 4196 is formed by air oxidation of DESH. It is believed to be a powerful vesicant, similar in effect to mustard (Small, 1983, cited in Rosenblatt, et al., 1995). In the middle and higher pH ranges additional reaction pathways contribute to the mix of hydrolysis products. In addition to P–S bond cleavage, the P–O–C bond to the ethoxy group and the C–S bond also are broken (Epstein, et al., 1974, cited in Rosenblatt, et al., 1995). The product of ethoxy group cleavage, EA 2192 is comparatively stable towards hydrolysis. Contrary to earlier opinion, Yang and coworkers (1992) demonstrated that up to 13% percent EA 2192 formed during the hydrolysis of VX even in aqueous 0.1 M NaOH. Szfraniec and coworkers who found that 17% EA 2192 formed in aqueous 2.0 M NaOH confirmed this (Szfraniec, et al., 1993, cited in Rosenblatt, et al., 1995). The C–S bond cleavage in the neutral pH range results in the formation of O-ethyl methylphosphonothioic acid, diisopropylaminoethyl sulfide and possibly other minor products (Epstein, et al., 1974, Yang, et al., 1990, cited in Rosenblatt, et al., 1995).

The ^{31}P NMR evidence confirms that in alcoholic NaOH VX reacts to form the sodium salts of EMPA and EA 2192 (Durst, et al., 1988). Table 3.1-10 summarizes the starting materials and final products in the alkaline hydrolysis of VX (Rosenblatt, et al., 1995).

Table 3.1-10. Products of Alkaline Hydrolysis of VX.

Principal Starting Materials	Principal Final Products
VX	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) DESH (2-diisopropylaminoethanethiol) EA 2192
	Product of air oxidation
	EA 4196 [Bis(2-diisopropylaminoethyl) disulfide] formed by the air oxidation of DESH
	Products formed closer to neutral pH
	O-ethyl methylphosphonothioic acid Diisopropylaminoethyl sulfide
Trace Starting Materials	**Trace Final Products**
N,N'-diisopropylcarbodiimide	N,N'-diisopropylurea
N,N'-dicyclohexylcarbidiimide	N,N'-dicyclohexylurea

A heat of reaction for the alkaline hydrolysis of VX was not found. VX hydrolysis rates are slower than those of the G-agents. A half-life of 2.5 hours has been reported for the hydrolysis of VX in water at pH 12 at 25° C (Epstein, et al., 1974, cited in Rosenblatt, et al., 1995).

According to Rosenblatt, it is extremely unlikely that VX, once hydrolyzed, would form again under any conditions (Rosenblatt, et al., 1995).

3.1.11 Chemical Neutralization of VX with Hypochlorite in Basic Solution

DPG routinely neutralizes VX with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the neutralization of VX in hypochlorite solution at a high pH. The source of hypochlorite ion may be NaOCl, HTH, or STB.

The reactions of hypochlorite with VX in basic solution have not been defined completely. With sufficient excess hypochlorite, the stoichiometry of the reaction has been reported as:

$$VX + 9\ NaOCl + 7\ NaOH \rightarrow$$
$$Na[EMPA] + \text{Diisopropyl amine} + 9\ NaCl + 5\ H_2O + Na_2SO_4 + 2\ Na_2CO_3$$

where: Na[EMPA] is the sodium salt of EMPA (Durst et al. 1988)

The ^{31}P NMR evidence indicates that VX forms the anion of EMPA plus a small amount of the anion of methylphosphonic acid in 5.25% NaOCl (Durst, et al., 1988). Table 3.1-11 (Rosenblatt, et al., 1995; Durst, et al., 1988) presents the starting materials and final products in the alkaline hydrolysis of VX in basic hypochlorite solution.

Table 3.1-11. Products of neutralization of VX in Sodium Hypochlorite Solution.

Principal Starting Materials	Principal Final Products
VX [O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothioate]	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) Sulfate, Carbonate, Chloride, and Diisopropyl amine
Trace Starting Materials	**Trace Final Products**
N,N′-diisopropylcarbodiimide	N,N′-diisopropylurea (possibly reversibly chlorinated)
N,N′-dicyclohexylcarbidiimide	N,N′-dicyclohexylurea (possibly reversibly chlorinated) Na[methylphosphonate]
OCl^-	Chlorate (ClO_3^-)

The reaction is exothermic, with a heat of reaction reported at "approximately -700,000 cal/mol for the reaction of VX with alkaline hypochlorite. The reaction rate in 10% HTH has been reported as ~ 70 seconds at 25° C (Yurow and Davis, 1982).

With the formation of sulfate, carbonate and diisopropylamine during the reaction of VX with hypochlorite, the chemical agent is completely disrupted and it is extremely unlikely that VX would form again under any conditions (Rosenblatt, et al., 1995).

3.1.12 Chemical Neutralization of Vx by Alkaline Hydrolysis

Vx is only slightly soluble in water at room temperature (Field Manual 3-9,1990). DPG neutralizes Vx with 10% aqueous NaOH, 10% NaOH in alcohol, 10% aqueous Na_2CO_3, and concentrated NH_4OH.

The hydrolysis of Vx is expected to proceed similarly to that of VX. Table 3.1-12 summarizes the presumed starting materials and final products in the alkaline hydrolysis of Vx. It is possible that Vx would require the addition of a stabilizer for long-term storage. It is not known whether a stabilizer was used with stored Vx.

Table 3.1-12. Products of Alkaline Hydrolysis of Vx

Principal Starting Materials	Principal Final Products
Vx	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) 2-dimethylaminoethanethiol The Vx analog of EA 2192
	Product of air oxidation
	The Vx analog of EA 4196 formed by the air oxidation of 2-dimethylaminoethanethiol
	Products formed closer to neutral pH
	O-ethyl methylphosphonothioic acid Dimethylaminoethyl sulfide
Trace Starting Materials?	**Trace Final Products?**
N,N′-diisopropylcarbodiimide	N,N′-diisopropylurea
N,N′-dicyclohexylcarbidiimide	N,N′-dicyclohexylurea

The hydrolysis rate for Vx may faster than that of VX because of the difference in molecular weight. By comparison to VX it is extremely unlikely that Vx, once hydrolyzed, would form again under any conditions.

3.1.13 Chemical Neutralization of Vx with Hypochlorite in Basic Solution

DPG neutralizes Vx with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the decontamination of Vx in hypochlorite solution at a high pH. The source of hypochlorite ion may be NaOCl, HTH, or STB.

The reactions of hypochlorite with Vx in basic solution are expected to be similar to those of VX. Table 3.1-13 summarizes the products of decontamination of Vx in NaOCl.

Table 3.1-13. Products of Neutralization of Vx in Sodium Hypochlorite Solution.

Principal Starting Materials	Principal Final Products
Vx [O-ethyl-S-(2-dimethylaminoethyl) methylphosphonothioate]	Na[EMPA] (sodium salt of ethyl methylphosphonic acid) Sulfate, Carbonate, Chloride, and Dimethyl amine
Trace Starting Materials?	**Trace Final Products?**
N,N´-diisopropylcarbodiimide	N,N´-diisopropylurea (possibly reversibly chlorinated)
N,N´-dicyclohexylcarbidiimide	N,N´-dicyclohexylurea (possibly reversibly chlorinated)
OCl^-	Chlorate (ClO_3^-)

By comparison to the reaction of VX with hypochlorite, the reaction of Vx with hypochlorite probably is rapid and exothermic. With the formation of sulfate, carbonate and dimethylamine during the reaction of Vx with hypochlorite, the chemical agent is completely disrupted and it is extremely unlikely that Vx would form again under any conditions.

3.1.14 Chemical Neutralization of H/HD with Hypochlorite in Basic Solution

HD is less than 1% soluble in water (Field Manual 3-9, 1990). DPG routinely neutralizes H/HD with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry. This discussion applies to the chemical neutralization of H/HD in hypochlorite solution at a high pH. The source of hypochlorite ion may be NaOCl, HTH, or STB.

Under optimum conditions (excess neutralization reagent, high pH, and adequate stirring) hypochlorite will oxidize H/HD to sulfate, chloride and carbon dioxide according to the following equation:

$$(ClCH_2CH_2)_2S + 14\ OCl^- \rightarrow SO4^{-2} + 16\ Cl^- + 4\ CO_2 + 4\ H^+ + 2\ H_2O$$

^{13}C NMR analysis of one such reaction mixture revealed greater than 99.5% destruction of HD and the formation of about 20 uncharacterized carbon-containing products. With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of mustard may persist (Durst, et al., 1988).

Little is known about the effect of hypochlorite upon the impurities produced during the manufacture of mustard. It is likely that conditions favorable to the complete mineralization of mustard to sulfate, chloride and carbon dioxide also will oxidize the additional sulfur atoms in the polysulfides. Other sulfur-containing impurities probably would be oxidized as well, if not to sulfate, at least to sulfoxides, sulfones or sulfonic acids (Rosenblatt, et al., 1995).

Table 3.1-14 presents the starting materials and final products in the alkaline hydrolysis of H/HD in basic hypochlorite solution (Rosenblatt, et al., 1995).

Table 3.1-14. Products of Neutralization of H/HD in Sodium Hypochlorite Solution.

Principal Starting Material	Principal Final Products
HD	Sulfate, chloride, and carbon dioxide
Other Starting Materials	**Other Final Products**
Impurities >1% reported in Mustard (H), or stored HD:	Expected to form sulfate, chloride, and carbon dioxide. If not, at least sulfoxides, sulfones or sulfonic acids
HD Disulfide in H	
1,4-Dithiane in H/HD	
HD Trisulfide in H	
1,2-bis(2-Chloroethylthio)ethane in H/HD	
1,2,3-Trithiolane in H	
1,4-Thioxane in H	
1,2-Dichloroethane in HD	
$S(CH_2CH_2CH_2Cl)_2$ isomers in HD	
OCl^- in H/HD	ClO_3^-

Yurow and Davis (1982) characterize the reaction of mustard with hypochlorite as "highly exothermic" (Yurow and Davis, 1982). Half-life data for the reaction were not found in this research. [DATA GAP]

With the formation of sulfate, chloride, and carbon dioxide during the reaction of HD with hypochlorite, there is no reason to expect its re-formation (Rosenblatt, et al., 1995).

3.1.15 Chemical Neutralization of HT with Hypochlorite in Basic Solution

The HT mixture is barely soluble in water (Field Manual 3-9, 1990). DPG routinely neutralizes HT with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH. This discussion applies to the neutralization of HT in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB.

T has not been studied as a separate agent. Its chemistry is very close to that of mustard and the neutralization reactions of mustard are expected to apply to HT with small differences attributable to solubility and reaction rates (Durst, et al., 1988). Therefore, under optimum conditions (excess neutralization reagent, high pH, and adequate stirring) hypochlorite is expected to oxidize HT as well as mustard to sulfate, chloride and carbon dioxide (Durst, et al., 1988).

3.1.16 Chemical Neutralization of HQ with Hypochlorite in Basic Solution

The HQ mixture is expected to behave similarly to the HT mixture. Because DPG neutralizes HT with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH, these neutralization solutions are expected to perform similarly for HQ.

Q has not been studied as a separate agent. Its chemistry is very close to that of mustard and the chemical neutralization reactions of mustard are expected to apply to HQ with small differences attributable to solubility and reaction rates. Therefore, under optimum conditions (excess neutralization reagent, high pH, and adequate stirring) hypochlorite is expected to oxidize HQ as well as mustard to sulfate, chloride and carbon dioxide.

3.1.17 Chemical Neutralization of HN-1 and HN-3 with Hypochlorite in Basic Solution

HN-1 and HN-3 are sparingly soluble in water, with HN-3 being the least soluble (Field Manual 3-9, 1990). DPG neutralizes HN-1 and HN-3 with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry.

Yurow and Davis (1982) reported that the only information found concerning aqueous oxidative neutralization of the nitrogen mustards was a reference to some exploratory studies.

3.1.18 Chemical Neutralization of L with Hypochlorite in Basic Solution

L is insoluble in water (Field Manual 3-9, 1990). DPG routinely neutralizes L with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry at a high pH. This discussion applies to the chemical neutralization of L in hypochlorite solution. The source of hypochlorite ion may be NaOCl, HTH, or STB.

Four substances have been found in stored L. L-1 is the primary component. L-2 is also a vesicant and may be present up to 10% or 20%. Some $AsCl_3$ is present as well (Yurow and Davis, 1982). L-3 is found in stored L. Smith and coworkers (1993) reported the analysis of a sample of distilled L. They found 95% trans isomer, <2% cis isomer, and 3% of a geminal isomer that has the chlorine attached to the carbon atom bonded to arsenic. The presence of the geminal isomer may explain Hewitt's report that

an isomer of L dissolved in cold NaOH without the evolution of acetylene and formed vinyl chloride when the solution was warmed to 40° C (Hewitt, 1948).

Most of the information discovered regarding the chemical neutralization of L focuses upon alkaline hydrolysis. When mixed with water L forms Lewisite oxide, ClCH=CHAsO, which goes on to polymerize. The aqueous solution of Lewisite oxide has vesicant properties (Durst, et al., 1988). The formation of Lewisite oxide is minimized or eliminated in an alkaline neutralization solution. The alkaline hydrolysis is written as:

$$ClCH{=}CHAsCl_2 + 6\ NaOH \rightarrow Na_3AsO_3 + 3\ NaCl + H_2C_2 + 3\ H_2O$$

(Yurow and Davis, 1982). The formation of acetylene is temperature and pH dependent. Waters and Williams reported that at 16° C the pH of a solution of L must be at least 10.5 to form acetylene, and that the pH must be at least 9 to form acetylene at 50° C (Waters and Williams, 1950).

Durst and coworkers (1988) cited a report by Buswell and Price (1944) that the reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation in solution, it offers no advantage over aqueous sodium hydroxide. According to Durst and coworkers (1988), the reaction of L with 5.25% NaOCl in aqueous solution proceeds as an alkaline hydrolysis, producing arsenite, chloride, and acetylene with the hypochlorite serving as a source of hydroxide. The ^{13}C NMR spectra confirm the rapid disappearance of L from the solution. Small traces of some uncharacterized carbon compounds remained. Evidently not much L-2 was present in the NMR sample. The evolution of acetylene was observed (Durst, et al., 1988). The hypochlorite will oxidize the arsenite (AsO_3^{-3}) to arsenate (AsO_4^{-3}).

Table 3.1-15 presents the starting materials and final products in the neutralization of L in basic hypochlorite solution (Yarow and Davis, 1982; Durst, et al., 1988; Smith, et al., 1993).

Table 3.1-15. Products of Neutralization of L in Sodium Hypochlorite Solution.

Principal Starting Material	Principal Final Products
L, or L-1	Acetylene, AsO^{-3}, and Chloride ion
Other Starting Materials	**Other Final Products**
L-2 and L-3	Probably Acetylene, AsO^{-3}, and Chloride ion
Geminal-Lewisite, (CH_2=CHClAsCl_2)	Vinyl chloride, and possibly AsO_4, and Chloride ion
$AsCl_3$	AsO^{-3}
OCl^-	ClO_3^-

The alkaline hydrolysis reaction has been reported as complete in less than 10 seconds with a heat of reaction of -102,000 cal/mol. L-2 appears to decompose more slowly in aqueous sodium hydroxide than does Lewisite (Yurow and Davis, 1982).

With the formation of acetylene during the reaction of L with hypochlorite there is no reason to expect its re-formation.

3.1.19 Chemical Neutralization of HL with Hypochlorite in Basic Solution

HL is a variable combination of HD and L that provides a mixture of low freezing point for use in cold weather operations or high-altitude spray (Field Manual 3-9, 1990). Because H and L are not very soluble in water the mixture is not expected to be soluble in water either. DPG neutralizes HL with 5% aqueous NaOCl, 10% aqueous HTH, and aqueous STB slurry.

Little information was found regarding the neutralization of HL mixtures specifically. Yurow and Davis (1982) recommended the use of 2-aminoethanol as a neutralization Solution for HL. The neutralization reactions of mustard and L in hypochlorite are expected to apply to HL.

3.1.20 Applicability of Chemical Neutralization as a Treatment Technology for Chemical Agent-related Waste Streams

The neutralization products for chemical agents presented in Section 3.1 are based on results from experiments performed in solution instead of chemical agent-related waste streams. The waste streams at DPG include solid materials that have been exposed to chemical agents. Much of the testing performed at DPG involves exposing a variety of materials to chemical agents. The exposure of impermeable, chemically unreactive substrates (such as stainless steel or glass) to chemical agents will result in minimal sorption of the agents. Painted metal is expected to absorb more, while plastics and elastomers would absorb even more. The neutralization solutions used do not penetrate permeable materials (paint, plastics, and elastomers), and additional time is required for the chemical agent to diffuse out of the permeable material into the neutralization solution. Once the chemical agent diffuses out of the permeable material into the neutralization solution its neutralization rate follows solution neutralization rates. The amount of agent absorbed by permeable substrates is a function of the concentration of agent and the time of exposure. The longer the delay between exposure of a permeable substrate to agent and the application of neutralization solution, the longer the neutralization process is expected to take (Rosenblatt, et al., 1995).

DPG chemical agent-related waste streams may also contain water-immiscible solvents such as chloroform or heptane. These solvents accumulate when standard solutions of agents or solutions of agent extracted from solid test items are discarded. In some situations, separate layers form in the

chemical neutralization vessel. DPG collects representative samples of the contents of liquid waste drums for agent analysis before disposal.

3.2 PERFORMANCE DATABASE

This section presents the DPG performance database. The performance database is the analytical results of chemical agent waste streams from DPG for approximately a 1-year period beginning March 27, 1997 through February 4, 1998. Chemical neutralization procedures used at DPG will be considered demonstrated if the data presented in the database indicate that the chemical agent concentration is less than the drinking water standard presented in Section 1.1. The sample descriptions provided in the database were taken directly from the description provided with the analytical sample. The database is presented as Table 3.2-1.

Table 3.2-1. Dugway Proving Ground Performance Database.

Sample Description	Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentrations							
			GA	GB	GD	GF	HD	HN-3	VX	L
HTH/soda ash decontamination	97-050, DUP	3/27/97	--	ND	--	--	--	--	--	--
Soda ash/nitric acid decontamination	97-063-1	4/8/97	--	ND	--	--	--	--	--	--
Water and soda ash, bleaches/rinses from chemical decontamination	97-063-2	4/8/97	--	ND	--	--	--	--	--	--
HTH/Nitric acid decontamination	97-063-3	4/8/97	--	ND	--	--	--	--	--	--
Waste, alcoholic caustic decontamination	97-068-1, 2	4/22/97, 4/29/97	--	--	ND	--	ND	--	ND	--
L bleach decontamination	97-080, DUP	5/16/97	--	--	--	--	--	--	--	ND
Bleach decontamination	97-081, DUP	5/15/97	--	ND	--	--	ND	--	--	--
Bleach decontamination	97-082	5/15/97, 5/16/97	--	--	ND	--	ND	--	ND	--
Bleach decontamination solutions	97-099, DUP	6/10/97, 6/24/97	ND	ND	ND	ND	ND	--	ND	--
Alcohol/caustic decontamination solutions	97-100, DUP	6/10/97, 6/24/97	ND	ND	ND	ND	ND	--	ND	--
Technicon nerve agent analysis waste, caustics/alcohols from chemical decontamination, liquid decontamination, analysis of VX waste, may contain water, acetate buffers, enzymes	97-110 A, B	7/19/97	--	--	--	--	--	--	ND	--
Spent bleach decontamination solutions, agent decontamination and rinses, may contain water, HTH, chloroform	97-111 A, B	7/16/97, 7/19/97	ND	ND	ND	ND	ND	--	ND	--
Water, bleach rinses decontamination agent bleach waste *GD, HD, VX*	97-112 A, B	7/16/97	--	--	ND	--	ND	--	ND	--
Water, bleach decontamination rinses (STB)	97-112 A, B	7/16/97	--	--	ND	--	ND	--	ND	--
Bleach waste, Technicon liquid, from technicon enzymatic analysis	97-113 A, B	7/19/97	--	--	--	--	--	--	ND	--
Bleach deconcontamination waste, liquid decontamination of VX waste, composite of 10 drums, may contain water, VX, HTH	97-113 C, D	7/19/97	--	--	--	--	--	--	ND	--
Waste, alcohol caustics solutions, alcohol caustic deconcontamination solutions, may contain water, acetone, isopropyl, alcohol	97-120 A, B	8/5/97, 8/6/97	--	ND	--	--	ND	--	ND	--
Waste bleach decontamination solutions, may contain water, HTH	97-121 A, B	8/5/97, 8/6/97	ND	ND	ND	ND	ND	--	ND	--
Waste alcohol/caustic, liquid caustic decontamination solutions, caustic alcohols for decontamination of GB, GF, may contain isopropyl alcohol, water, sodium hydroxide	97-130 A, B	8/25/97	--	ND	--	ND	--	--	--	--
Alcohol/caustic decontamination solution, liquid, alcohol caustic decontamination solution of GB, GF, may contain isopropyl alcohol, ethanol, water	97-131 A, B	8/25/97	--	ND	--	ND	--	--	--	--
Alcohol/caustic waste decontamination solution, caustic liquid decontamination solution, agent decontamination with caustic solutions	97-138 A, B	9/15/97, 9/17/97	ND	ND	ND	ND	ND	--	ND	--
Waste, Lewisite bleach decontamination solution, liquid	97-139 A, B	9/11/97	--	--	--	--	--	--	--	ND
Liquid bleach decontamination solution, agent decontamination with bleach solutions	97-140 A, B	9/15/97, 9/17/97	ND	ND	ND	ND	ND	--	ND	--
Bleach decontamination solution, water, solids: PPE, glass, chem-wipes	97-147 A, B	9/25/97, 9/29/97	ND	ND	ND	ND	ND	--	ND	--
Alcohol/caustic solid/liquid comination: PPE, glassware, chem-wipes, plastic bags, alcohol/caustic decontamination of solids and liquids	97-153 A, B	10/20/97	ND	ND	ND	ND	ND	--	ND	--
Liquid bleach decontamination of L, may contain calcium, *hypochlorite, water L decontamination*	97-156 A, B	10/20/97	ND	ND	ND	ND	ND	--	ND	ND
Bleach decontamination of solid/liquid combination	97-161 A, B	10/29/97, 10/30/97	ND	ND	ND	ND	ND	--	ND	--
Liquid bleach decontamination of L, from decontamination of hoses, the history of which showed all agents including L, may contain bleach, water, traces of alcohol	97-162 A, B	11/29/97, 11/30/97	ND	ND	ND	ND	ND	--	ND	ND
Liquid bleach decontamination, solid/liquid combination waste, decontamination with bleaches of agents which are test generated	97-167 A, B	11/4/97, 11/6/97	ND	ND	ND	--	ND	--	ND	--
DP55, liquid/solid, decontamination of solids and liquids exposed to agents through testing, solids and liquids in alcohol/caustic decontamination solutions	97-175 A, B	12/8-11/97	ND	ND	ND	ND	ND	--	ND	--

Table 3.2-1. Dugway Proving Ground Performance Database.

Sample Description	Chemical Laboratory Number	Chemical Laboratory Analysis Date	Reported Chemical Agent Concentrations							
			GA	GB	GD	GF	HD	DIN-3	VX	L
Liquid/solid, decontamination of agents and solid items with bleachs	97-178 A, B	12/8-11/97	ND	ND	ND	ND	ND	--	ND	--
Solid/liquid combination, alcohol/caustics, generated through the decontamination with caustics process	98-004 A, B	1/29/98	ND	ND	ND	ND	ND	--	ND	--
Bleach deconcontamination of solid/liquid combination waste, generated through lab clean-up	98-011 A, B	2/4/98	ND	ND	ND	ND	ND	--	ND	ND
Bleach decontamination process waste, solid/liquid from multiple tests	98-012A, B	2/4/98	ND	ND	ND	ND	ND	--	ND	--

-- Not Analyzed
ND Not Detected
Detection limits are the same concentration as the U.S. Army's drinking water standards.
Detection limits are based on chemical agent in brine and are as follows.
GA 0.02 milligrams/liter (mg/L)
GB 0.02 mg/L
GD 0.02 mg/L
VX 0 02 mg/L
HD 0.2 mg/L
L 2 0 mg/L

4.0 SUMMARY AND CONCLUSIONS

This section summarizes the evaluation for each of the categories of the chemical agent neutralization procedures that are routinely used at DPG and concludes whether the chemical neutralization procedure as an LDR treatment technology is applicable. These summaries and conclusions are based on the evaluation categories presented in Section 3.1 and demonstrated using the DPG performance database presented in Section 3.2. These summaries and conclusions are presented in the following tables:

The order of the summary and conclusion tables are as follows:

- Table 4.0-1 Alkaline Hydrolysis of GA
- Table 4.0-2 Alkaline Hypochlorite Neutralization of GA
- Table 4.0-3 Alkaline Hydrolysis of GB
- Table 4.0-4 Alkaline Hypochlorite Neutralization of GB
- Table 4.0-5 Alkaline Hydrolysis of GD
- Table 4.0-6 Alkaline Hypochlorite Neutralization of GD
- Table 4.0-7 Alkaline Hydrolysis of GF
- Table 4.0-8 Alkaline Hypochlorite Neutralization of GF
- Table 4.0-9 Alkaline Hydrolysis of VX
- Table 4.0-10 Alkaline Hypochlorite Neutralization of VX
- Table 4.0-11 Alkaline Hydrolysis of Vx
- Table 4.0-12 Alkaline Hypochlorite Neutralization of Vx
- Table 4.0-13 Alkaline Hypochlorite Neutralization of H/HD
- Table 4.0-14 Alkaline Hypochlorite Neutralization of HT
- Table 4.0.15 Alkaline Hypochlorite Neutralization of HQ
- Table 4.0-16 Hypochlorite Neutralization of HN-1 and HN-3
- Table 4.0-17 Alkaline Hypochlorite Neutralization of L
- Table 4.0-18 Alkaline Hypochlorite Neutralization of HL

Table 4.0-1. Alkaline Hydrolysis of GA.

Evaluation Category	
General chemistry & NMR Data	Experimental evidence confirms the identity of the primary products of the alkaline hydrolysis of GA as Na[ethyl dimethylaminophosphonate] and NaCN. Products from the hydrolysis of the known impurity are present in low concentration.
Thermodynamics & Kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of agent is not expected.
Performance Database	The performance database contains five samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GA, if the cyanide ion is kept below acceptable levels. Alkaline hydrolysis neutralization of GA has been demonstrated at DPG.

Table 4.0-2. Alkaline Hypochlorite Neutralization of GA.

Evaluation Category	
General chemistry & NMR Data	The sodium salt of the phosphonate ion resulting from the alkaline hypochlorite neutralization of GA is the primary product of this reaction. The cyanide ion is destroyed by hypochlorite. This research did not confirm the fate of the dimethylamino group. Reaction products from the known impurity are present in low concentration. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion and kinetic considerations suggest that the reaction is sufficiently rapid.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution cyanide ion is destroyed and the re-formation of agent is not possible.
Performance Database	The performance database contains 12 samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GA. Alkaline hypochlorite neutralization of GA has been demonstrated at DPG.

Table 4.0-3. Alkaline Hydrolysis of GB.

Evaluation Category	
General chemistry & NMR Data	A large body of experimental evidence confirms the identity of the primary products of alkaline hydrolysis of GB are Na[IMPA] and NaF. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics & Kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of agent is not expected.
Performance Database	The performance database contains two samples where this neutralization procedure has been used at DPG in the past year
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GB. Alkaline hydrolysis neutralization of GB has been demonstrated at DPG.

Table 4.0-4. Alkaline Hypochlorite Neutralization of GB.

Evaluation Category	
General chemistry & NMR Data	Experimental evidence confirms the identity of the primary products of alkaline hypochlorite neutralization of GB to be the same as those from alkaline hydrolysis. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of agent is not expected.
Performance Database	The performance database contains seven samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GB. Alkaline hypochlorite neutralization of GB has been demonstrated at DPG.

Table 4.0-5. Alkaline Hydrolysis of GD.

Evaluation Category	
General chemistry & NMR Data	Experimental evidence confirms the primary products of alkaline hydrolysis of GD are Na[PMPA] and NaF. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics & Kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid. An organic solvent may be added to the neutralization solution to increase the solubility of GD.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of agent is not expected.
Performance Database	The performance database contains six samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hydrolysis is applicable to the neutralization of GD. Alkaline hydrolysis neutralization of GD has been demonstrated at DPG.

Table 4.0-6. Alkaline Hypochlorite Neutralization of GD.

Evaluation Category	
General chemistry & NMR Data	Experimental evidence confirms the identity of the primary products of alkaline hypochlorite neutralization of GD to be the same as those from alkaline hydrolysis, Na[PMPA] and NaF. Reaction products from the known impurities are present in low concentration. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion and kinetic considerations suggest that the reaction is sufficiently rapid. An organic solvent may be added to the neutralization solution to increase the solubility of GD.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of agent is not expected.
Performance Database	The performance database contains 15 samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite neutralization is applicable to the neutralization of GD. Alkaline hypochlorite neutralization of GD has been demonstrated at DPG.

Table 4.0-7. Alkaline Hydrolysis of GF.

Evaluation Category	
General chemistry & NMR Data	Little experimental evidence was found regarding the products of the alkaline hydrolysis of GF. The products of hydrolysis of GF are expected to be similar to the products of hydrolysis of the related agents, GB and GD. The products of hydrolysis of probable additives and impurities are expected to be present in low concentrations.
Thermodynamics & Kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic considerations indicate that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of GF in water.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of chemical agent is not expected.
Performance Database	The performance database contains seven samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Based upon the similarity of GF to GB and GD, alkaline hydrolysis is considered applicable to the neutralization of GF. Alkaline hydrolysis of GF has been demonstrated at DPG.

Table 4.0-8. Alkaline Hypochlorite Neutralization of GF.

Evaluation Category	
General chemistry & NMR Data	Little experimental evidence was found regarding the products of the neutralization of GF in alkaline hypochlorite. By comparison with the reactions of the related agents, GB and GD, the products of hydrolysis of GF are expected to be similarly innocuous. Products of hydrolysis of probable additives and impurities are present in low concentrations. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	By comparison with GB, thermodynamic considerations suggest that the neutralization reaction proceeds to completion and kinetic considerations suggest that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of GF in water.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of agent is not expected.
Performance Database	The performance database contains 11 samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Hypochlorite neutralization is applicable to the neutralization of GF. Alkaline hypochlorite neutralization of GF has been demonstrated at DPG.

Table 4.0-9. **Alkaline Hydrolysis of VX.**

Evaluation Category	
General chemistry & NMR Data	There is convincing evidence that the principal products of the alkaline hydrolysis of VX are the sodium salt of ethyl methylphosphonic acid, DESH and EA 2192. DESH can be air oxidized to EA 4196. Products from the hydrolysis of known additives and impurities are present in low concentration.
Thermodynamics & Kinetics	Thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Kinetic considerations indicate that the reaction is sufficiently rapid.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of VX is not expected.
Performance Database	The performance database contains eight samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Because the possible formation of EA2192 and EA4196, alkaline hydrolysis is not the preferred neutralization procedure for VX. Alkaline hydrolysis of VX has been demonstrated at DPG.

Table 4.0-10. **Alkaline Hypochlorite Neutralization of VX.**

Evaluation Category	
General chemistry & NMR Data	The neutralization reaction of VX in alkaline hypochlorite has not been characterized completely. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of VX is not possible.
Performance Database	The performance database contains 17 samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite neutralization is applicable to the neutralization of VX. Alkaline hypochlorite neutralization of VX has been demonstrated at DPG.

Table 4.0-11. Alkaline Hydrolysis of Vx.

Evaluation Category	
General chemistry & NMR Data	By comparison to VX it is expected that the principal products of the alkaline hydrolysis of Vx are the sodium salt of ethyl methylphosphonic acid, the Vx analogs of DESH and EA 2192. The Vx analog of DESH may be air oxidized to the Vx analog of EA 4196. Products from the hydrolysis of known additives and impurities are expected to be present in low concentration.
Thermodynamics & Kinetics	By comparison to VX, thermodynamic considerations suggest that the neutralization reaction proceeds to completion. Similar kinetic considerations indicate that the reaction is sufficiently rapid.
Re-formation of Agent	Under conditions of alkaline hydrolysis in dilute solution the re-formation of Vx is not expected.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Because of the possible formation of the Vx analogs of EA2192 and EA4196, alkaline hydrolysis is not the preferred neutralization procedure for Vx.

Table 4.0-12. Alkaline Hypochlorite Neutralization of Vx.

Evaluation Category	
General chemistry & NMR Data	The neutralization reaction of Vx in alkaline hypochlorite has not been characterized. Reaction products from the known impurities are present in low concentration. Reaction products from the known additives may include low concentrations of reversibly chlorinated ureas. Excess hypochlorite can form chlorate upon standing.
Thermodynamics & Kinetics	By comparison with VX, thermodynamic considerations predict that the neutralization reaction proceeds to completion and comparable kinetic measurements suggest that the reaction is sufficiently rapid.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of Vx is not expected.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite neutralization is expected to be applicable to the neutralization of Vx. Alkaline hypochlorite neutralization of Vx has not been demonstrated at DPG, however results are expected to be similar to results forVX.

Table 4.0-13. Alkaline Hypochlorite Neutralization of H/HD.

Evaluation Category	
General chemistry & NMR Data	In the presence of excess neutralization solution, at high pH and with adequate stirring, alkaline hypochlorite will oxidize HD to sulfate, chloride and carbonate. A variety of uncharacterized compounds remain at low concentration after neutralization. Impurities probably are oxidized in a similar manner.
Thermodynamics & Kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic data were not found.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of HD is not possible. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of HD in water.
Performance Database	The performance database contains 16 samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of HD. Alkaline hypochlorite neutralization of HD has been demonstrated at DPG.

Table 4.0-14. Alkaline Hypochlorite Neutralization of HT.

Evaluation Category	
General chemistry & NMR Data	The neutralization of HT in alkaline hypochlorite has not been characterized. Agent T is very similar to HD and is expected to give the same products as HD in the alkaline hypochlorite neutralization.
Thermodynamics & Kinetics	Thermodynamic and kinetic data were not found. Based upon the similarity of T to HD, the reaction is expected to proceed in the same way. Additional allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of T in water.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of HD or T are not expected.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of HT. Alkaline hypochlorite neutralization of HT has not been demonstrated at DPG, however results are expected to be similar to results for HD.

Table 4.0-15. Alkaline Hypochlorite Neutralization of HQ.

Evaluation Category	
General chemistry & NMR Data	The neutralization of HQ in alkaline hypochlorite has not been characterized. Agent Q is very similar to HD and is expected to give the same products as HD in the alkaline hypochlorite neutralization.
Thermodynamics & Kinetics	Thermodynamic and kinetic data were not found. Based upon the similarity of Q to HD, the reaction is expected to proceed in the same way. Additional allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of Q in water.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution the re-formation of HD or Q are not expected.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of HQ. Alkaline hypochlorite neutralization of HQ has not been demonstrated at DPG, however results are expected to be similar to results for HD.

Table 4.0-16. Hypochlorite Neutralization of HN-1 and HN-3.

Evaluation Category	
General chemistry & NMR Data	No experimental evidence was found to support the applicability of hypochlorite neutralization to HN-1 and HN-3.
Thermodynamics & Kinetics	No thermodynamic or kinetic data were found.
Re-formation of Agent	No information regarding the re-formation of HN-1, HN-2, and HN-3 from neutralization solutions was found.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Consider hypochlorite neutralization not applicable to HN-1 or HN-3 until supporting information is found. Hypochlorite neutralization of HN-1 or HN-3 has not been demonstrated at DPG.

Table 4.0-17. Alkaline Hypochlorite Neutralization of L.

Evaluation Category	
General chemistry & NMR Data	L-1 and its isomers are converted to acetylene, arsenite, and chloride in the presence of base. In the presence of alkaline hypochlorite the arsenite is converted to arsenate. L-2 and L-3 are expected to form the same products. A trace of geminal L, if present, forms vinyl chloride, arsenate, and chloride.
Thermodynamics & Kinetics	Thermodynamic considerations predict that the neutralization reaction proceeds to completion. Kinetic measurements confirm that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of L in water.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution acetylene is formed and the re-formation of the L is not possible.
Performance Database	The performance database contains five samples where this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of L. Alkaline hypochlorite neutralization of L has been demonstrated at DPG.

Table 4.0-18. Alkaline Hypochlorite Neutralization of HL.

Evaluation Category	
General chemistry & NMR Data	The neutralization of HL in alkaline hypochlorite has not been characterized. The reaction is expected to proceed as parallel HD and L neutralizations.
Thermodynamics & Kinetics	Thermodynamic considerations suggest that the neutralization reactions would proceed to completion. Kinetic considerations suggest that the reaction is sufficiently rapid. Allowance may need to be made (longer time for neutralization or use of an organic solvent) for the low solubility of HD and L in water.
Re-formation of Agent	Under the conditions of hypochlorite neutralization in dilute alkaline solution and the re-formation of the agents are not expected.
Performance Database	The performance database contains no evidence that this neutralization procedure has been used at DPG in the past year.
Conclusions	Alkaline hypochlorite is applicable to the neutralization of HL. Alkaline hypochlorite neutralization of HL has not been demonstrated at DPG, however results are expected to be similar to results for HD and L.

5.0 REFERENCES

AGEISS Environmental, Inc. (AGEISS). 1997, September. Chemical Agent Waste Management Plan.

Angelotti, M., W. H. Rice, and H. J. Vogt. 1955, October. A Search for Potential Thickeners for GB: Selection and Study of UCON 75-H-90,000. U.S. Army Dugway Proving Ground. Dugway, UT.

Bassam J.J., G. Chettur, R.J. Dihu, M. Schurger, and R. H. Snow. 1983, May 30. Development of Chemical Processes for Chemical Demilitarization – Phase I, Final Phase I Report for Period 1 July 1982 – 30 April 1983, Prepared for U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Edgewood Area, Aberdeen Proving Ground, MD. Report DRXTH-TE-CR-83209.

Beaudry, W.T., J. H. Buchanan, D. K. Rohrbaugh, J. B. Samuel, L. L. Szafraniec, and J. R. Ward. 1993, January. Analysis of Decontamination Solutions of G Agents to Detect Reformation of Agent. Research and Technology Directorate. ERDEC-TR-005 Edgewood Research, Development, and Engineering Center.

Burck, G., J. Bane, R. W. Mengel, J. Williamson, J. Stevens, and K. Gardner. 1992, November. Chemical Weapons Process Parameters, Volume 2 – Data Appendices. Defense Nuclear Agency, Alexandria, VA. DNA-TR-910217-V2.

Davis, G.T., F. Block, J.D. Gorrell, and J. Epstein. 1977, March. Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components. U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD. EC-TR-76101.

Davis, P.M., R.L. Kipp, M.E. Brooks, and M.L. Duggan. 1979, April. Decontaminating Solution for the Disposal of Identification and Training Sets. Army Armament Research and Development Command, Aberdeen Proving Ground, MD.

Department of the Army Pamphlet 385-61. 1997, March. Toxic Chemical Agent Safety Standards. Headquarters, Department of the Army. Washington, D.C.

Durst, H.D., E.W. Sarver, H.W. Yurow, W.T. Beaudry, P.A. D'Eramo, D.M. Jackson, H. Salem, J.B. Samuel, L.L. Szafraniec, F. P. Ward, and J. R. Ward. 1988, November. Support for the Delisting of Decontaminated Liquid Chemical Surety Materials As Listed Hazardous Waste from Specific Sources. CRDEC-TR-009, Research Directorate, November 1988.

Field Manual 3-9. 1990. Potential Military Chemical/Biological Agents and Compounds. Headquarters, Departments of the Army, Navy, and Air Force. Washington, D.C. FM3-9.

Franke, S. 1967. Manual of military Chemistry, Volume I – Chemistry of Chemical Warfare Agents. Headquarters, Department of the Army. CN-787-67.

Hewitt, C.L. 1948. Isomers of 2-Chlorovinyldichloroarsine *in* J. Chem. Soc. 1203-1205.

Jackson, K. E., and M. A. Jackson. 1935. The Chlorovinylarsines *in* Chem. 16:429-452.

Mcandless, J.M and V. Fedor. 1992, October. Destruction and Waste Treatment Methods Used in a Chemical Agent Disposal Project. Defence Research Establishment, Suffield Ralston, Alberta, Canada.

Operation Plan. 1978, March. Range Clearance of Dugway Proving Ground Hazardous Areas, Appendix B, Description of Agents. Dugway Proving Ground, Dugway, UT.

Rosenblatt, D.H., M.J. Small, T.A. Kimmel, and A.W. Anderson. 1995, October. Agent/Decontamination Chemistry Technical Report. U.S. Army Test and Evaluation Command.

Saftey Office, U.S. Army CRDEC, revision of June 1995. Material Safety Data Sheet for HQ. U.S. Army Chemical, Research, Development, and Engineering Center, Aberdeen Proving Ground, MD.

Samuel, J. B., W. T. Beaudry, D. K. Rohrbaugh, L. L. Sfraniec, A. B. Butrow, L. R. Procell, D. C. Sorrick, and Y. C. Yang. 1998, January. Agent Neutralization Study II: Detoxification of HD with Aqueous Bleach. Research and Technology Directorate. ERDCE-TR-458.

Smith, J.R., T.P. Logan, L.L. Szafraniec, and E.M. Jakubowski. 1993. Identification of the Isomeric Forms of Lewisite Using Mass Spectrometry, NMR and IR Spectroscopy, and Molecular Modeling. 1993 Medical Defense Biosciences Review Proceedings, Volume 1, May 10-13, 1993. U.S. Army Medical Research and Development Command. p. 351-360.

Technical Manual 3-215. 1963, December. Military Chemistry and Chemical Agents. Departments of the Army and the Air Force, Washington, D.C.

U.S. Army Medical Research Institute of Chemical Defense. 1995, September. Medical Management of Chemical Casualties Handbook (2nd ed.) Chemical Casualty Care Office. Aberdeen Proving Ground, MD.

Waters, W.A., and J.H. Williams. 1950. Hydrolyses and Derivatives of Some Vesicant Arsenicals *in* J. Chem. Soc. 18-22.

Yang, Y.-C., J.A. Baker, and J.R. Ward. 1992. Decontamination of Chemical Warfare Agents, *in* Chem. Rev. 92: 1729-1743.

Yurow, H.W. and G.T. Davis. 1982, November. Decontamination and Disposal Methods for Chemical Agents – A Literature Survey. U.S. Army Armament Research and Development Command. Aberdeen Proving Ground, MD. ARCSL-TR-81080

Yurow, H.W. 1988, November. Decontamination of Chemical Agents GA, GB, GD, HD, L, and VX A Literature Survey (1918-1987). Chemical Research, Development, & Engineering Center. Aberdeen Proving Ground, MD. CRDEC-SP-88020.

BACKGROUND DOCUMENT FOR CHEMICAL NEUTRALIZATION AS A LAND DISPOSAL RESTRICTION TREATMENT TECHNOLOGY FOR CHEMICAL AGENT ASSOCIATED WASTE

APPENDIX A

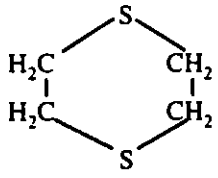
CHEMICAL STRUCTURES DICTIONARY

APPENDIX A

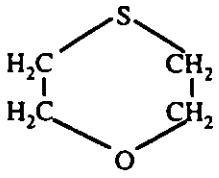
CHEMICAL STRUCTURES DICTIONARY

Appendix A contains the chemical structures dictionary. This dictionary contains the chemicals discussed in the report.

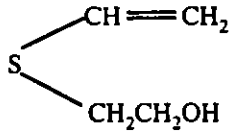
APPENDIX A
Chemical Structures Dictionary



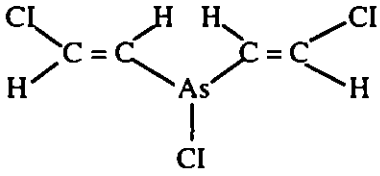
1,4 - Dithiane



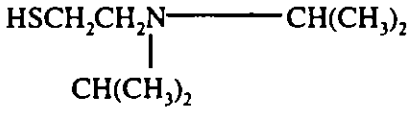
1,4 - Oxathiane



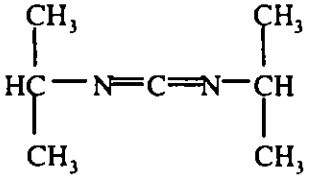
2 - Vinylthioethanol



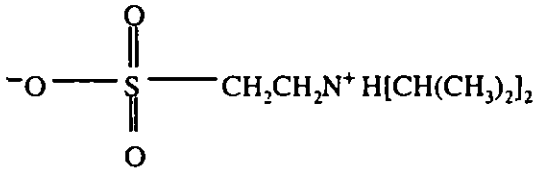
bis-(2-chlorovinyl) chloro arsine
or L-2



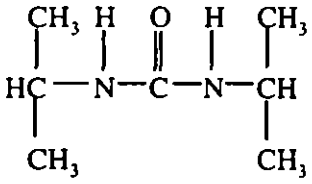
DESH



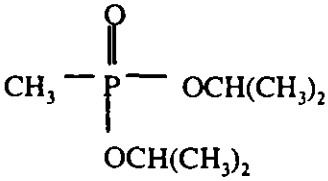
N,N′-Diisopropyl
Carbodiimide



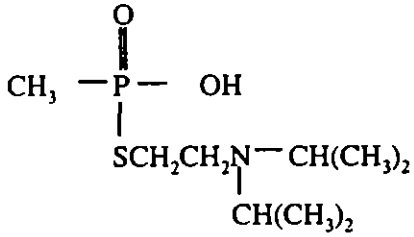
Diisopropyltaurine



N,N′-Diisopropylurea

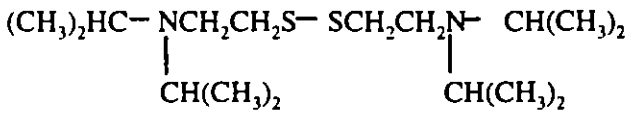


DIMP

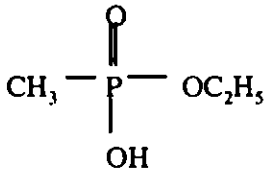


EA 2192

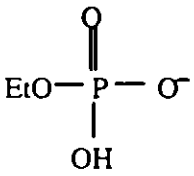
APPENDIX A
Chemical Structures Dictionary



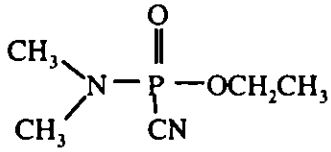
EA 4196 OR $(DES)_2$



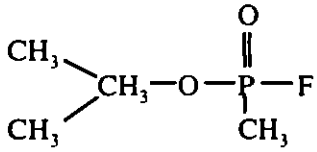
EMPA



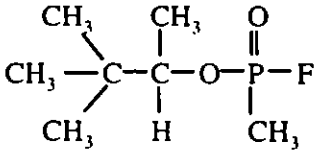
Ethyl ester of phosphonic acid, anion form



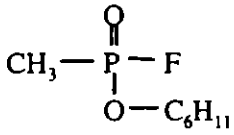
GA



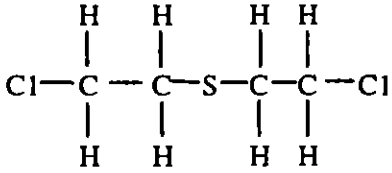
GB



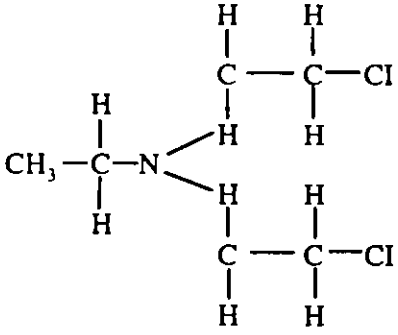
GD



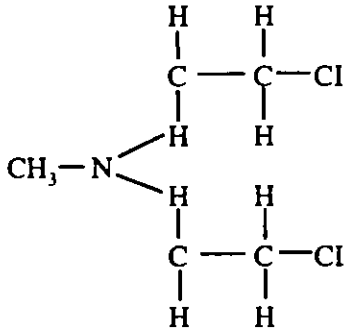
GF



H/HD

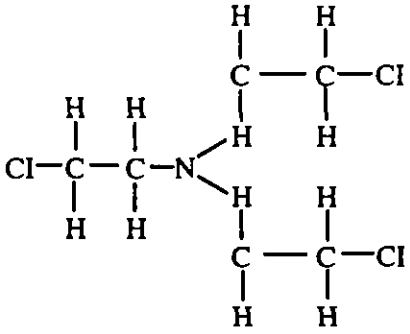


HN-1

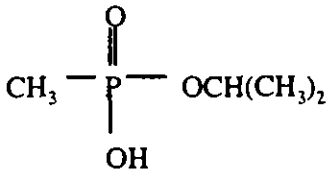


HN-2

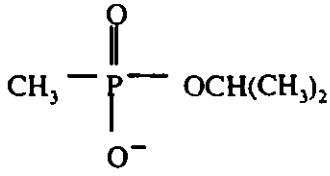
APPENDIX A
Chemical Structures Dictionary



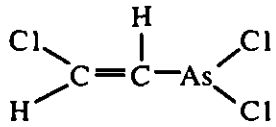
HN-3



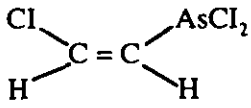
IMPA



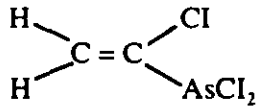
IMPA Anion



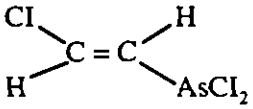
L



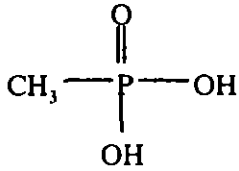
cis-Lewisite



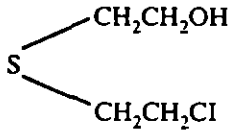
geminal-Lewisite



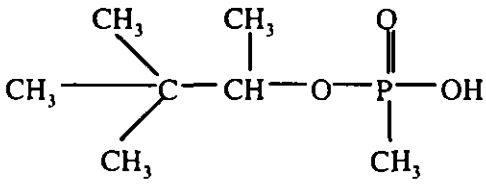
trans-Lewisite



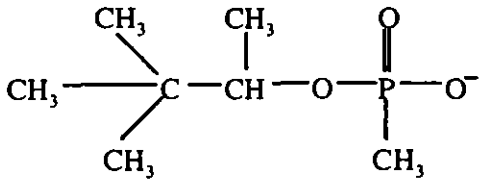
MPA



Mustard Chlorohydrin

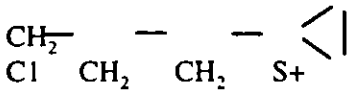


Pinacolylmethyl phosphonic acid

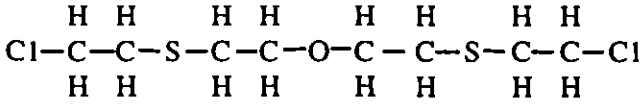


Pinacolylmethyl phosphonic acid anion

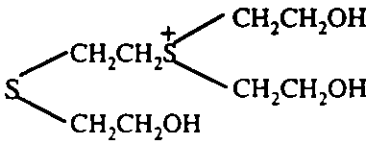
APPENDIX A
Chemical Structures Dictionary



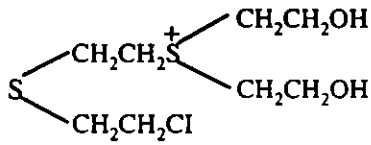
Sulfonium Ion Intermediate



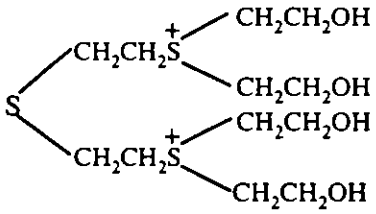
T



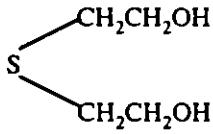
CH-TG



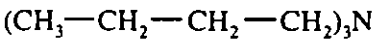
H-TG



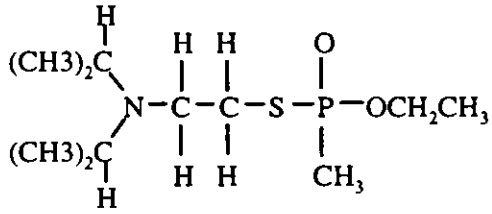
H-2TG



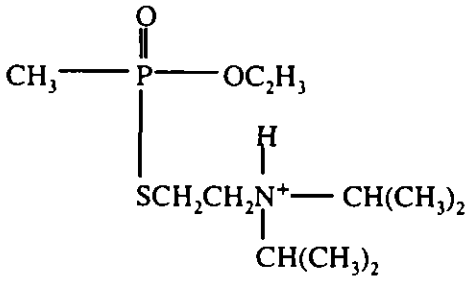
Thiodiglycol



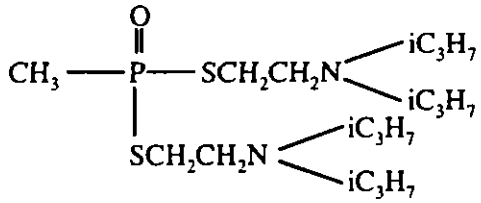
Tributylamine



VX

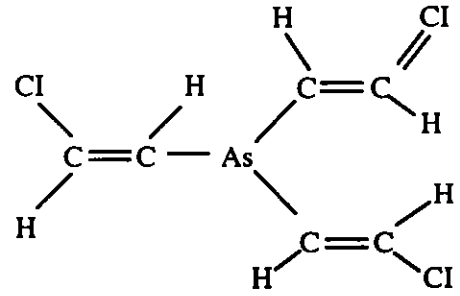


Protonated VX

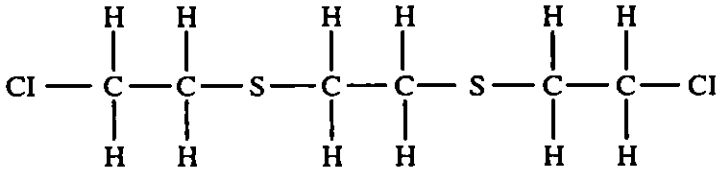


"Bis Impurity" in VX

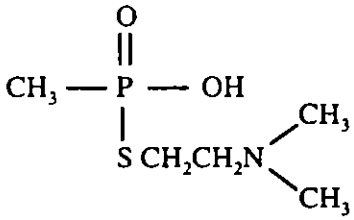
APPENDIX A
Chemical Structures Dictionary



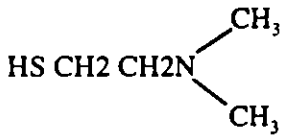
L-3 or Tris(2-chlorovinyl) arsine



Q



Vx Analog of EA2192



Vx Analog of DESH

EDGEWOOD RESEARCH, DEVELOPMENT & ENGINEERING CENTER

ERDEC-TR-005

ANALYSIS OF DECONTAMINATION SOLUTIONS OF G AGENTS TO DETECT REFORMATION OF AGENT

William T. Beaudry
James H. Buchanan
Dennis K. Rohrbaugh
John B. Samuel
Linda L. Szafraniec
J. Richard Ward

RESEARCH AND TECHNOLOGY DIRECTORATE

January 1993

U.S. ARMY
CHEMICAL
AND BIOLOGICAL
DEFENSE AGENCY

Aberdeen Proving Ground, Maryland 21010-5423

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1993 January	Final, 91 Dec - 92 Mar

4. TITLE AND SUBTITLE

Analysis of Decontamination Solutions of G Agents to Detect Reformation of Agent

5. FUNDING NUMBERS

PR-10161102A71A

6. AUTHOR(S)

Beaudry, William T.; Buchanan, James H.; Rohrbaugh, Dennis K.; Samuel, John B.; Szafraniec, Linda L.; and Ward, J. Richard

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

DIR, ERDEC,* ATTN: SCBRD-RTC, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER

ERDEC-TR-005

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*When this work was performed, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center (CRDEC), and the authors were assigned to the Research Directorate.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Agents from a full scale binary munition test were decontaminated with caustic in a 300 gal holding tank. Analysis of the contents by standard methods revealed a trace amount of G agent present despite the highly caustic solution. A technical review of the analytical methods was carried out to determine if the G agent was actually present or an artifact of the analysis.

A literature search revealed similar concerns when brine solutions from nerve agent decontamination were analyzed using similar analytical methods. This study concluded that nerve agents reformed at reduced pH or in chloroform extracts of the neutralized or slightly acidic brines. Experiments using nuclear magnetic resonance (NMR), gas chromatography (GC), and GC/mass spectrometry (GC/MS) were used to see where, if any, G agent was present during the analysis. Results obtained confirmed G agent reforming in either the neutral aqueous solution or in the chloroform extract but not in chloroform extracts of the caustic solution. No agent was detected using methylene chloride as the extraction solvent as recommended by the earlier study.

14. SUBJECT TERMS			15. NUMBER OF PAGES
G agent	Decontamination	Demilitarization	27
Chloroform	Analytic chemistry	Mass spectrometry	16. PRICE CODE
Fluoride ion	Gas chromatography	(Continued on page 2)	

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

PREFACE

The work described in this report was authorized under Project No. 10161102A71A, Research CW/CB Defense. This work was started in December 1991 and completed in March 1992.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public.

*When this work was performed, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center, and the authors were assigned to the Research Directorate.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ANALYSIS OF DECONTAMINATION SOLUTIONS OF G AGENTS TO DETECT REFORMATION OF AGENT

1. INTRODUCTION

Recent analyses revealed trace amounts of agent in a 300 gal holding tank that contained a caustic aqueous solution used to decontaminate G agents. Under such conditions, G agents are expected to rapidly hydrolyze to form O-alkyl methylphosphonic acid and fluoride ion.[1] Subsequent hydrolysis occurs much more slowly to form methylphosphonic acid and the corresponding alcohol. The unexplained and surprising presence of agent in this solution raised the possibility that unexpected reactions besides simple hydrolysis were taking place. The possibility that unexpected reactions were occurring raised the issue that our standard laboratory decontaminating procedures submitted to the State of Maryland[2] might be incomplete. It is also important to resolve this anomaly, because similar analytical procedures may be used to verify destruction of chemical stockpiles under a chemical-weapons treaty.

To probe deeper into the source of the agent in the decontamination bath, Chemical Division personnel [U.S. Army Chemical Research, Development and Engineering Center (CRDEC)*] worked with Analytical Division (CRDEC) analysts to look at each step of the analyses to identify unusual reactions taking place. Chemical Division personnel also reviewed the literature for similar anomalies in the analyses of chemical agents.

Before discussing the analyses of the ingredients in the holding tank, the recent history of the use of the tank should be reviewed.

The holding tank is located in the toxic chamber that is used for full-scale testing of chemical systems, including fills for binary munitions. The agents produced or used in testing are transferred to the holding tank for decontamination. For G agents, solid sodium hydroxide is added to an aqueous solution of the agent to hydrolyze it into innocuous O-alkyl methylphosphonic acid salts and fluoride ion. The holding tank may also contain catalysts used in the binary tests, various polymers tested as thickeners, and solvents such as 1-methyl-2-pyrrolidinone used to dissolve thickened agent from surfaces in the test chamber.

Test records showed that approximately 112 kg of agent had been added over a period of time to the holding tank. Solid sodium hydroxide, as well as water, was added to keep the solution caustic and to maintain the volume at 300 gal. A total of 600 lb of solid sodium hydroxide was added before the analyses that revealed the presence of agent.

The toxic chamber was closed for some months for a safety-related investigation. During this time, salts and a solid mass had precipitated from the originally homogeneous solution. This led to speculation that the

*On 1 October 1992, CRDEC became the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC).

evidence of trace G agent in the supernatant liquid could possibly be related to the heterogeneous mixture in the tank. Against this background, repeat analyses were done of the supernatant liquid, as well as a portion of the solid polymeric mass, to see if agent could have become occluded.

The original analyses of the supernatant liquid started by neutralizing the sample to pH 4-5 with concentrated hydrochloric acid followed by extraction with chloroform. The chloroform extract was then injected into a gas chromatograph (GC), where the presence of agent was inferred from the retention times of the peaks in the chromatogram. Thus, the questions to be addressed were whether the peaks from the GC were actually agent and, if so, was the agent present in the caustic supernatant liquid or did the agent possibly reform during the neutralization or extraction.

A brief literature review revealed that a major effort was conducted during the 1970s to resolve a similar anomaly encountered during neutralization and incineration of the resultant brine from spray drying GB.[3-5] One set of authors[3] concluded that the presence of trace amounts of agent from the neutralized brine resulted from reformation of agent. This conclusion arose from the observation that the amount of agent detected was greater with chloroform than other organic solvents, and more agent was detected from a neutral solution than from a caustic solution.

To ascertain whether the analyses of the holding tank were subject to the same uncertainties as the analyses of the brines, the analyses of the holding tank were repeated. The analyses used the recommended protocol from the earlier work[3] and nuclear magnetic resonance (NMR) spectroscopy was used to monitor reactions and products in the aqueous solutions as well as in the organic extracts. Analyses by gas chromatography/mass spectrometry (GC/MS) and GC were also done to try to confirm the presence of the agent by alternate techniques. Individual summaries of the GC, GC/MS, and NMR results are presented and are followed by a discussion summarizing our overall results, with comments on how these results fit with existing reaction schemes for organophosphorus esters.

2. GAS CHROMATOGRAPHY (GC)

2.1 Experimental Procedures.

An HP 5880A (Hewlett Packard, Avondale, PA) GC equipped with a flame ionization detector (FID) was used for this work. Analyses were accomplished using a 30 m fused silica capillary column (0.32 mm ID) with a 0.25 μm film of methylsilicone (SE-30). The carrier gas was helium split at a 50:1 ratio. Pressure controlled (47 KPa) column flow resulted in a calculated helium flow of 22.7 cm/s (1.1 mL/min) based on the retention gap (2.2 min) obtained for methane at 40 °C. Detector make-up flow was helium at a rate of 23 mL/min. The injection port temperature was 225 °C and the detector temperature was 325 °C. The column oven temperature was programmed from 75 to 300 °C at 20 °C/min. The combustion gases were hydrogen and air, at 32 and 420 mL/min, respectively. The septum purge flow was adjusted to 1 mL/min. A Hamilton 7001SN microliter syringe (Hamilton, Reno, NV) was used to manually

inject 1.0 μL sample volumes. Area integration of the resulting chromatographic peaks was accomplished electronically.

The FID minimum detectable level (MDL) for each of the alkyl methylphosphonofluoridates was determined to be 2 ng with a signal of better than twice the noise level for a 1.0 μL injection in chloroform. An agent standard, traceable to the Chemical Agent Standard Analytical Reference Material (CASARM) program, was obtained from Steven Pleva (Analytical Division, CRDEC) for this determination. Because the most volatile alkyl methylphosphonofluoridate co-eluted with the decontamination co-solvent, 1-methyl-2-pyrrolidinone (N-methyl pyrrolidinone), under the chromatographic conditions previously described, GC monitored the least volatile alkyl methylphosphonofluoridate component for presence or absence of agent at the MDL for all water samples. No interferences were observed in this immediate area (±0.2 min).

2.2 Results.

2.2.1 Liquid Phase Samples.

Four samples of the liquid phase from the toxic chamber (Samples 26323-A, 260061-A, 26006-1B, and 26006-1C) were received for GC characterization. Because these water samples were all determined to be at pH >13, direct injection into the GC was not attempted. Initial attempts to isolate and then to detect the agent in these caustic solutions involved extraction with chloroform. All results were negative using ratios of 2:1, and 5:1 (Sample to $CHCl_3$). However, when the caustic water samples were acidified with HCl and then extracted with chloroform at a 50:1 ratio, a peak corresponding to alkyl methylphosphonofluoridate was detected at levels above the MDL. Substitution of methylene chloride as the extraction solvent yielded negative results for the presence of agent suggesting that agent was being reformed as a result of sample preparation and handling, using chloroform and acidification.

2.2.1.1 Chloroform Extracts of Caustic Water Samples.

Sample 26323-A was submitted and run on 20 December 1991. Organic compounds were extracted by the addition of 0.5 mL $CHCl_3$ to 1.0 mL of the water sample. Multiple 1.0 μL injections of the organic extract were negative for the anticipated alkyl methylphosphonofluoridate at or above the MDL. The agent standard eluted at 6.36 min under the GC conditions. A peak eluting at 6.15 min in the water sample extract was determined not to be the agent in question by spiking 0.25 mL of the water sample extract with 0.05 mL of the agent standard. Baseline separation of both peaks resulted.

On 7 January 1992, organic compounds were extracted from Sample 26323-A by adding 0.5 mL $CHCl_3$ to 2.5 mL of the water sample. Injection of 1.0 μL of the extract was negative for the anticipated agent at the MDL. The MDL was rechecked and again determined to be at 2 ng for each agent. Retention times were also rechecked at this time; they were consistent with previous runs. Sample 26323-A was spiked with the agent standard (5:1), and

the resulting chromatogram indicated complete separation of the 6.15 min water sample extract peak and the 6.36 min alkyl methylphosphonofluoridate peak.

With the GC system verification accomplished, Samples 260061-B and 260061-C were extracted in chloroform (5:1, Sample to $CHCl_3$). Multiple 1.0 μL injections of the organic extract from each were negative for the anticipated alkyl methylphosphonofluoridate at or above the MDL.

2.2.1.2 Chloroform Extracts of Acidified Water Samples.

Samples 260061-A, 260061-B, and 260061-C were extracted in chloroform at 50:1, Sample to $CHCl_3$, after acidification with HCl and characterized by GC. Using the instrumentation and procedures previously described, all three samples were positive for the anticipated alkyl methylphosphonofluoridate at or above the MDL, and it was possible to determine qualitatively the samples' relative order of agent concentration based on the GC data. The assumptions were made that all three samples were handled in the same manner and that the extraction efficiency was the same.

Sample 260061-C was the least concentrated, because the anticipated alkyl methylphosphonofluoridate was detected at levels barely above the MDL. Electronic integration of the GC peak, corresponding to the agent of interest, was not accomplished because the peak was not large enough to overcome the threshold of the integrator's level of detection. Therefore, the peak was not integrated.

Sample 260061-A showed slightly more agent than Sample 260061-C. Electronic integration of the GC peak, corresponding to the agent of interest, yielded 2.5 area counts.

Sample 260061-B was the most concentrated of the three because the anticipated alkyl methylphosphonofluoridate peak was detected at levels significantly above the MDL. Electronic integration of the GC peak, corresponding to the agent of interest, yielded 5.1 area counts.

2.2.2 Polymer Phase Sample.

Sample 263231-C was submitted and run by GC. This sample was a chloroform extract from a representative sample of the polymer phase of the chamber holding tank. Multiple 1.0 μL injections of the organic extract were negative for the anticipated alkyl methylphosphonofluoridate at or above the MDL.

2.3 Discussion.

The GC results corroborate the positive reading for G agent in the chloroform extract, but the results suggest that the agent is reforming in either the acidified aqueous solution or in the chloroform. The presence of agent from decontaminated G agent solution is identical to the problem encountered in the 1970s,[3] where the decontaminated solution was acidified and extracted with chloroform.

3. GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

3.1 Experimental Procedures.

3.1.1 Materials.

Seven samples were received from the Analytical Systems Group, Analytical Research Division (CRDEC), for GC/MS characterization. Chamber Samples 26323-A, 26006-1B, and 26006-1C were received as liquid aqueous samples, pH >13. All three samples were extracted at this pH into chloroform (1 mL sample to 0.5 mL chloroform for Sample 26323-A; 2.5 mL sample to 0.5 mL chloroform for Samples 26006-1B and 26006-1C). Three chamber samples (26006-1A, 26006-1B, and 26006-1C) were received as chloroform extracts from the Analytical Systems Group (CRDEC). These samples had been acidified to pH 5.5 prior to extraction with chloroform (150 mL sample to 3 mL chloroform, 50:1 extraction ratio). Chamber Sample 26006-1E was received as polymer isolated from the chamber sample. The solid material (2.64 g) was taken as received, chopped into small pieces, and sonicated in 10 mL of distilled water for 1 h. The polymer was removed from the water by syringe filtration and the water extracted with 0.5 mL methylene chloride (5.3:1 extraction ratio).

A 161 ppm agent standard prepared by the Analytical Systems Group (CRDEC) from agent obtained from the CASARM program was used to obtain calibration curves for quantitation.

3.1.2 Experimental Procedures.

3.1.2.1 Full Scan GC/MS/CI.

Chloroform and methylene chloride extracts of the chamber samples were analyzed using a Finnigan 5100 GC/MS equipped with a 15 m x 0.25 mm DB-5 capillary column (J&W Scientific Company, Rancho Cordova, CA). The oven was programmed from 60 to 260 °C at 10 °C/min. Injection port temperature was 200 °C, and the GC/MS interface temperature was 220 °C. An injection of 0.5 µL of each extract was injected in the splitless mode. Samples were analyzed in the chemical ionization (CI) mode using methane as the reagent gas (0.5 Torr). Masses were scanned from 60 to 300 amu at 1 scan/s. Under these conditions, the base peak for one agent occurs at m/z 85 and the base peak for another agent occurs at m/z 97. One phosphonofluoridate elutes at 162 and 165 s (2 peaks), and the less volatile agent elutes at 316 and 318 s (2 peaks). The first agent could not be detected in the chamber sample extracts at the levels present because coelution occurs with 1-methyl-2-pyrrolidinone, which is the major component in the extraction samples (96-98% of the total extraction product). The detection limit using full scan GC/MS for each injected extract was 2 ppm for the less volatile agent.

3.1.2.2 Selected Ion Mode GC/MS.

To obtain maximum sensitivity for agent detection, masses were also scanned in the selected ion monitoring (SIM) mode from 96.5 to 97.5 amu. Total scan time in this mode was 1.1 s with an agent detection limit of 0.2 ppm for each extract injected.

3.1.2.3 Quantitation.

The concentration of the less volatile agent in the chamber samples was obtained using full scan and SIM GC/MS, depending on the agent concentration in the extract. For full scan quantitation, standards containing the less volatile agent at concentrations of 2 ppm and 13.5 ppm were run before and after the sample extracts. Extracts were diluted 5:1 with chloroform, if necessary, (Samples 26006-1A and 26006-1B, pH5, 50:1 extraction ratio) so that concentrations for all samples fell within this range. To reduce interference from other contaminants, quantitation was obtained by taking the area under the peak in the m/z 97 ion chromatogram.

If no agent was detected above 2 ppm in the extracts, SIM, which provides a detection limit of 0.2 ppm, was applied. Greater variability was observed in the SIM runs. The sensitivity was dependent upon the electrometer zero (EZ) setting, which drifts throughout the day. For this reason, the EZ setting was adjusted between each run and replicate runs were obtained. Sample 26006-1B, pH >13 (3 runs), and Sample 26006-1C, pH >13 (5 runs), were quantitated using standards containing the less volatile agent at concentrations of 0.25 ppm (5 runs), 0.5 ppm (4 runs), and 0.75 ppm (2 runs). Quantitative results were obtained using the most sensitive run in each case and by using average values, obtaining the same results in each case. In addition, each extract was spiked with 0.25 ppm agent. Quantitation of the spiked samples gave excellent agreement with the previously obtained results.

Rough quantitation of the other compounds detected in the extracts was obtained by comparison of GC peak areas to those for the agent and making the assumption that all compounds have the same detector response. Differences in extraction efficiencies were not taken into account.

3.2 Results.

3.2.1 Liquid Phase Samples.

3.2.1.1 Basic Samples.

Three samples were extracted as received (pH >13) into chloroform. As shown in Table 1, no agent was detected in chamber Sample 26323-A (detection limit 100 ppb). Traces of the less volatile agent were observed in Samples 26006-1B (100 ppb) and 26006-1C (43 ppb). The more volatile agent is possibly present in similar concentrations but is obscured by the large 1-methyl 2-pyrrolidinone peak. The major component detected in the extracts accounting for 98% of the total product was 1-methyl-2-pyrrolidinone . Other compounds observed by GC/MS were the alcohol derived from the less volatile agent (15 ppm), 1,3-diisopropylurea (0.4-0.8 ppm), and the 3 alkyl alkylmethylphosphonates (diesters) expected from the two agents (total concentration, 45-78 ppm). Trace amounts of diesters resulting from an alcohol impurity were also observed (<1 ppm). A complete list of compounds detected is shown in Table 2. A GC/MS chromatogram for sample 26006-1B is shown in Figure 1.

TABLE 1
Agent Concentrations Observed in Chamber Sample Extracts by GC/MS

Sample	Sample pH Before Extraction	Extraction Solvent	Extraction Ratio	Agent, ppb[a]	
				Extract[b]	Chamber Sample
26323-A (liquid)	>13	$CHCl_3$	2:1	<200	<100
26006-1B (liquid)	>13	$CHCl_3$	5:1	500	100
26006-1C (liquid)	>13	$CHCl_3$	5:1	215	43
26006-1A[c] (liquid)	5	$CHCl_3$	50:1	21,500	430
26006-1B[c] (liquid)	5	$CHCl_3$	50:1	46,500	930
26006-1C[c]	5	$CHCl_3$	50:1	4,000	80
26006-1E (polymer)	--	CH_2Cl_2	5.3:1	<200	<40

[a] Does not include the more volatile agent which is not detected because it coelutes with 1-methyl-2-pyrrolidinone. The more volatile agent is probably also present in concentrations approximately equal to those listed above.

[b] Detection limit of 200 ppb.

[c] Extraction done by Analytical Systems Group.

TABLE 2
Summary of Compounds Detected in Chamber Sample 26006 By Full Scan GC/MS

R.T. (sec)	Compound	Estimated PPM in Original Sample[1]					
		Liquid pH 5			Liquid pH>13		Polymer
		1A	1B	1C	1B	1C	1E
84	Agent Alcohol Impurity	0.2	0.2	0.2	0.1	—	—
102	Agent Alcohol	8.3	5.4	3.4	14.6	14.6	7.5
302	1,3-Diisopropylurea	3.2	4.3	4.5	0.4	0.8	0.3
319	Agent[b]	0.3	0.9	0.08	--	--	--
352	Unknown MW 138	--	0.1	0.08	--	--	--
457	Unknown MW 137	0.1	0.2	0.2	--	--	--
510	Diester	0.4	1.5	0.3	5.5	7.6	2.0
625	Mixed Diester Impurity	--	0.1	0.07	0.5	0.4	--
666	Mixed Diester	1.4	3.9	0.7	40.2	26.6	4.2
784	Agent Diester Impurity	--	0.02	0.01	0.4	--	--
815	Agent Diester	1.0	1.8	0.3	32.4	11.5	5.4

[a] Quantitation does not include 1-methyl-2-pyrrolidinone and impurities which account for 96-98% of the total extracted product.

[b] Less Volatile Agent. The more volatile agent is probably also present in similar amounts but is not detected because it coelutes with 1-methyl-2-pyrrolidinone.

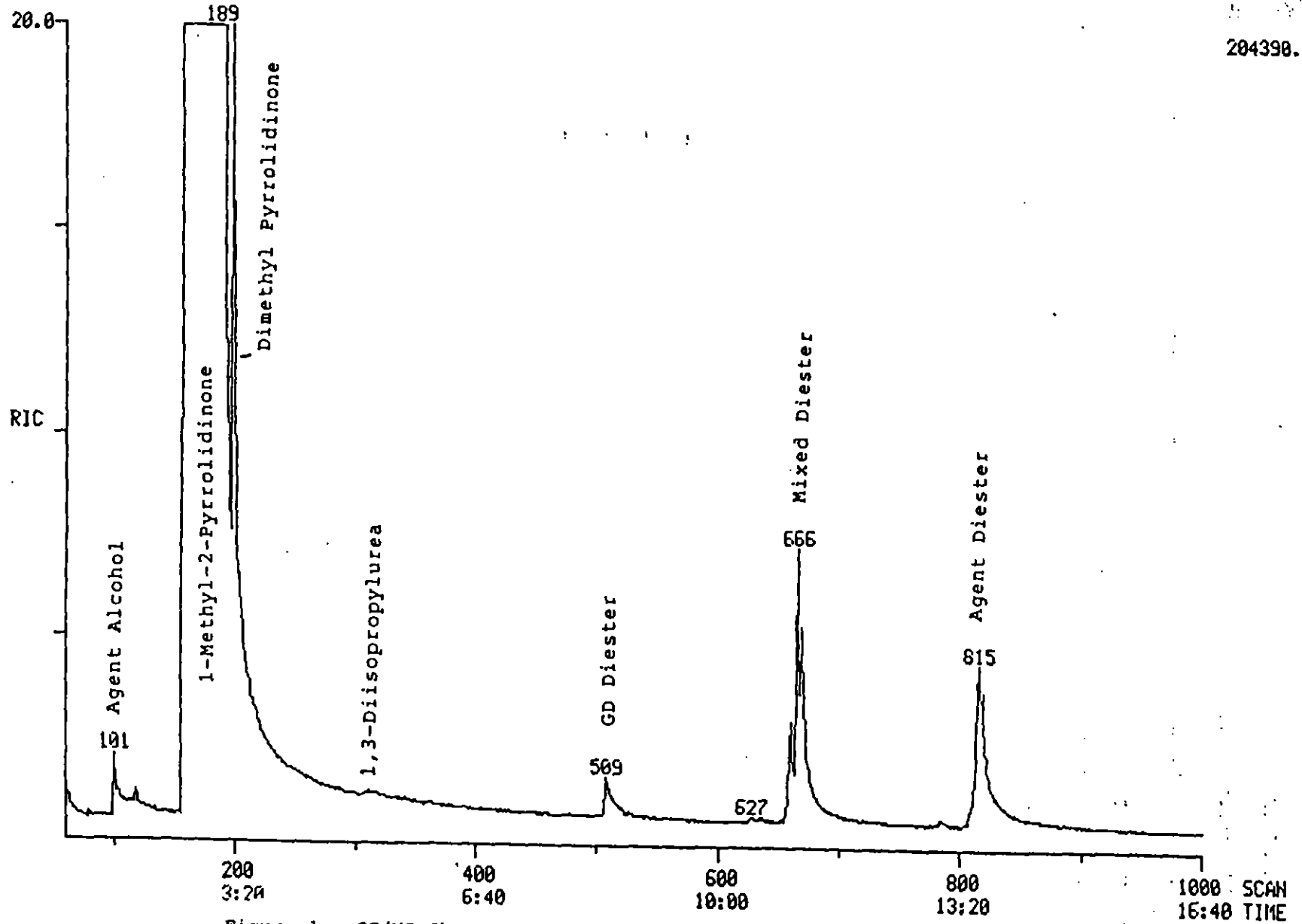


Figure 1. GC/MS Chromatogram of 26006-1B Chloroform Extract (5:1, pH>13)

3.2.1.2 Acidic Samples.

Chloroform extracts of chamber Samples 26006-1A, 26006-1B, and 26006-1C were analyzed as received. These samples had previously been neutralized to pH 5 before extraction into chloroform (150 mL sample to 3 mL chloroform). Concentrations of the less volatile agent detected in 1a, 1b, and 1c were an order of magnitude higher than that observed for the basic samples and were 430 ppb, 930 ppb, and 80 ppb, respectively, as shown in Table 2. Assuming the more volatile agent is also present in similar concentrations, the total agent concentration in these samples would be 0.9 ppm, 1.9 ppm, and 0.2 ppm, respectively. As with the basic samples, 1-methyl-2-pyrrolidinone accounted for 98% of the total ion chromatogram. Other compounds observed were the same as in the basic samples but in different ratios and included the alcohol derived from the less volatile agent (3-8 ppm), 1,3-diisopropylurea (3-5 ppm), and the 3 diesters (1-7 ppm). The detection of the urea suggests that the stabilizer diisopropylcarbodiimide was initially present in the binary starting material. A complete list of compounds detected is shown in Table 1 and a GC/MS chromatogram for Sample 26006-1B is shown in Figure 2.

3.2.1.3 Polymer Phase Sample.

Polymer Sample 26006-1E (2.64g) was chopped into small pieces, extracted with water (10 mL), and then extracted into methylene chloride (0.5 mL) rather than chloroform. No agent was detected using SIM (40 ppb detection limit). The polymer sample was used as received and probably contained a small amount of liquid. Other compounds observed by GC/MS were similar to those observed in the liquid and are shown along with estimated concentrations in Table 2.

3.3 Discussion.

The GC/MS data also confirm the presence of agent in the chloroform extract from the acidic aqueous solution and in the chloroform extract of the caustic solution. No agent was seen in the chloroform extract of the caustic decontamination solution with GC alone. Note, however, that the amount detected by GC/MS in the caustic solution extract was below the detection limit of the GC. However, the agent seen in the chloroform extract of the pH4 aqueous solution shows that some formation of agent is occurring. The amount of agent in the extract of the acidified solution is an order of magnitude greater than the amount in the extract from the caustic supernatant liquid. The earlier studies in the 1970's[3] also noted traces of agent in the chloroform extracted directly from the caustic solution. Such extracts always contained much smaller amounts of agent than predicted from the amount of agent in the chloroform extracted from the neutralized solution. This ambiguity led workers to recommend that methylene chloride be used for extraction in lieu of chloroform.

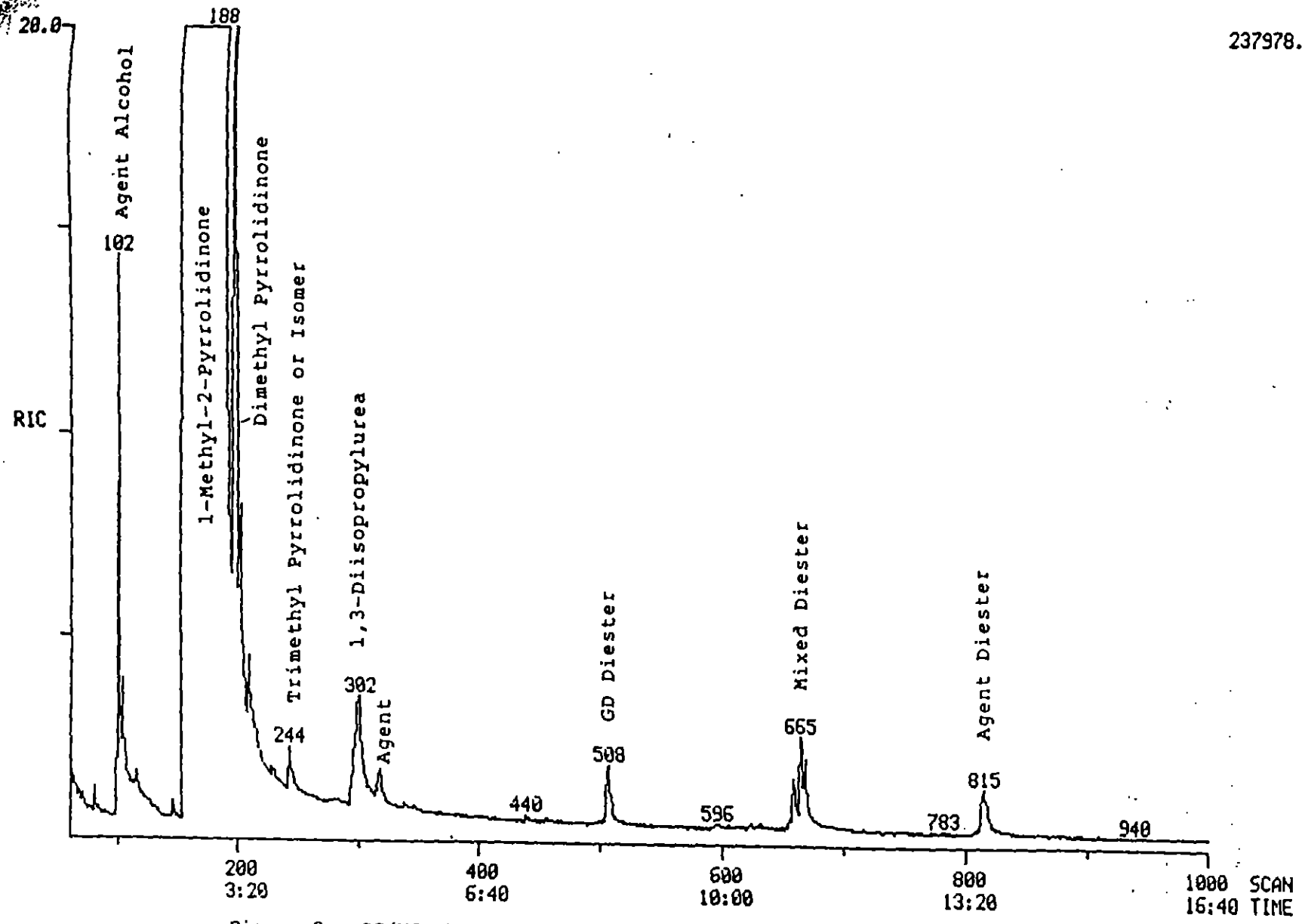


Figure 2. GC/MS Chromatogram of 26006-1B Chloroform Extract (50:1, pH 5)

4. NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

4.1 Experimental Procedures.

The Analytical Systems Group, Analytical Research Division (CRDEC), prepared and submitted the samples which were used as received. Approximately 1 mL of sample was placed into a clean, 5-mm o.d. Pyrex NMR tube. The tube was capped with a pressure cap, and the top of the tube was wrapped with Parafilm.

The ^{19}F and ^{31}P NMR spectra were recorded using a Varian VXR-400S superconducting FTNMR system. The ^{19}F spectra were recorded at 376 MHz using a sweep width of 100 KHz, a pulse width of 23-35 μs (74-90°), an acquisition time of 0.6 s, and a pulse delay of 1.5-2.5 s. The ^{31}P NMR spectra were recorded at 162 MHz using a sweep width of 40 KHz, a pulse width of 8.6 μs (57°), an acquisition time of 0.8 s, a pulse delay of 2.5 s, and gated proton WALTZ decoupling. All spectra were recorded at probe temperature (ca. 22 °C), and quantitative data were obtained by digital integration of the peak areas of interest. The number of repetitions for each sample was determined by the signal-to-noise ratio required or desired for that sample.

4.2 Results.

4.2.1 Liquid Phase Samples.

4.2.1.1 Basic Samples.

Three samples of the liquid from the toxic chamber (Samples 26323-A, 26006-1B, and 26006-1C) were characterized as received (pH >13, colorpHast indicator strip pH 0-14) using ^{31}P NMR spectroscopy. The three samples were the same, consisting of 80 mol % of alkyl methylphosphonic acids, 19 mol % methylphosphonic acid (MPA), and smaller amounts of various dialkyl methylphosphonates (diesters, 0.2-0.7 mol %) various other CH_3-P acids/pyros, fluorophosphoric acid (0.03 mol %), and other phosphates (Table 3). Qualitatively, these liquid samples appeared concentrated in phosphorus compounds. Based on our previous experience with spectra of similar samples "quenched" 10 parts aqueous decontaminating solution to 1 part agent (alkyl methylphosphonofluoridate), these chamber samples were at least as concentrated as a 9 Vol % solution of the agent. These results are consistent with the nominal dilution of agent in the 300 gal tank.

Because all three chamber samples were identical via ^{31}P NMR, Sample 26006-1B was chosen for evaluation by ^{19}F NMR. The ^{19}F spectrum of the liquid phase as it exists in the holding tank contained mainly fluoride ion, as expected. Also, fluorophosphoric acid and the PF_6^- anion were observed (Table 4). The PF_6^- anion was not detected by ^{31}P NMR because its resonance at δ-144 ppm was outside the spectral window. Using the amount of fluorophosphoric acid as an "internal standard," the amount of fluoride ion present in solution appears to be ca. 16.8% of that which is expected. This is only a rough estimate, because the ^{19}F NMR spectra are only semi-quantitative, being

Table 3. ^{31}P NMR Results for the Toxic Chamber Samples

Sample No.	$CH_3P(=O)(OR)(OH)$	$CH_3P(=O)(OH)_2$	$CH_3P(=O)(OR)_2$	$CH_3P(=O)(OR)F$	$(CH_3P(=O)(OH)-)_2O$	$CH_3P(=O)(OR)(OH/H)$	$FP(=O)(OH)(OH)$	Other Phosphates	Remarks
26323-A pH 14 12/19/91 - Neat	80.36	19.17	0.23	-	0.04	0.14	0.02	0.04	
26006-1B pH 14 1/6/92 - Neat	79.79	19.29	0.68	-	0.05	0.11	0.04	0.04	
26006-1C pH 14 1/7/92 - Neat	79.44	19.67	0.58	-	0.04	0.15	0.04	0.07	
26006-1B pH 4.5 1/15/92 - $CHCl_3$ xtr	99.07	-	-	0.16	-	-	-	-	Diesters (ca .2%) under acid peak.
26006-1A pH 4.5 1/22/92 - Neat	80.96	18.70	0.21	-	0.03	0.05	0.04	-	
26006-1A pH 4.5 2/3/92 CH_2Cl_2 xtr	86.5	-	3.5	-	-	10.1	-	-	
Polymer Phase (13% in CH_2Cl_2) 2/5/92	55.8	12.8	-	-	-	31.5	-	-	Peaks broad.

Table 4. ^{19}F NMR Results for the Toxic Chamber Samples

Sample No.	F^-	$CH_3P(O)(OR)F$	PF_6^-	$CH_3P(O)(OH)F$	$FP(O)(OH)OH$	$FP(O)(OR)OH$	Other	Remarks
26006-1B pH 4.5 1/15/92 $CHCl_3$ xtr	9.4	83.2	2.5	-	-	-	4.9	
26006-1B pH 14 1/16/92 Neat	99.63	-	0.24	-	0.12	-	-	Spiked with 1 ppm TFA and 20 ppm GD
26006-1A pH 4.5 1/22/92 Neat	92.87	-	0.34	0.17	0.20	-	6.42	Overnight accumulation. Other includes fluorinated carbon compounds.
26006-1A pH 4.5 1/24/92 Neat	95.00	-	0.32	0.13	0.20	0.03	4.33	3 day accumulation. Other includes fluorinated carbon compounds.
Polymer Phase 13wt% CH_2Cl_2 1/30/92	98.92	-	0.63	-	0.45	-	-	Peaks very broad.
26006-1A pH 4.5 1/30/92 CH_2Cl_2 xtr	-	-	100	-	-	-	-	S/N = 39/1
26006-1A pH 12.88 2/6/92 $CHCl_3$ xtr	-	-	77.3	-	-	-	22.7	

run mainly for detectability of low level compounds rather than for rigorous quantitation. However, the results do indicate that most of the fluorine may have precipitated out of solution as NaF or as amine fluoride salt.

Because there was no way to determine if detectability in the ^{19}F spectra was adequate to observe fluorine at the 1 ppm level, the chamber sample was spiked with 1 ppm trifluoroacetic acid (TFA) and rerun. A spectrum from data accumulated for 3 days showed a single resonance (S/N = 40/1) for the TFA. Because TFA contains three equivalent fluorines and no proton coupling and because the alkyl methylphosphonofluoridates of interest exist as diastereomers and are coupled to phosphorus as well as four protons, 1-2 ppm of agent quite possibly would not be observed. Consequently, this same chamber sample (26006-1B, pH >13) was spiked with 20 ppm GD (CASARM Lot# GD-U-6157-CTF-N), a quantity definitely detectable under the experimental conditions. A similar 20 ppm sample of GD in distilled water was also prepared. After 1 h of data accumulation, the four resonances for the GD diastereomers were observed in the water sample (δ58.1 and 60.0, J_{P-F} = 1051 Hz). Data for the spectrum of the spiked chamber sample was accumulated overnight increasing the signal-to-noise ratio for the spectrum by a factor of 3 over the GD/water sample. No agent was observed; the GD apparently hydrolyzed in the chamber sample.

A chloroform extract of the basic sample (pH 12.88) was also characterized by ^{19}F NMR. Only the presence of PF_6^- and an unidentified compound were detected. No other resonances indicating the presence of methylphosphonofluoridates were observed.

4.2.1.2 Acidified Samples.

To extract the agent into chloroform for analyses by GC, the aqueous chamber samples are acidified with HCl. The ^{31}P NMR spectrum of the acidified chamber sample (26006-1A, pH ca. 5.5, colorpHast indicator strip pH 0-14) showed that the phosphorus-containing compounds were essentially unchanged by acidifying the sample (Table 3). On the other hand, the ^{19}F spectrum of the acidified sample indicated that fluorination reactions were occurring in the aqueous medium. The PF_6^- anion and the fluorophosphoric acid observed in the sample at pH >13, the presence of methylphosphonofluoridic acid (fluor acid, 0.34%) and two other organofluorine compounds, as well as the fluoride ion, were observed 1 day after acidification. Three days later, small amounts of two alkylfluorophosphates (0.03%) were observed that indicated fluorination of some species in the sample was continuing. Presumably, the fluor acid could result from the displacement of the alkoxy group by fluorine in the alkyl methylphosphonic acids, the major phosphorus compounds present. Similarly, the alkylfluorophosphates could be formed by reaction of fluorine with any dialkylphosphates that may be present. Because several dialkyl methylphosphonates (diesters) are present at pH >13 and pH ca. 5.5, one might expect to see the alkyl methylphosphonofluoridates (agent) form from the displacement of one alkoxy moiety by fluorine. However, after 3 days of data accumulation, no agent could be detected in the ^{19}F NMR spectrum of the acidified chamber sample.

When this acidified sample was extracted with chloroform (150 mL of sample to 3 mL of chloroform) and essentially concentrated by a factor of 50, the various diastereomers of the expected alkyl methylphosphonofluoridates were observed in the chloroform extract by ^{31}P and ^{19}F NMR. The ^{31}P spectrum showed that the major phosphorus compounds present in the chloroform extract were still the alkyl methylphosphonic acids, 99.07% (Table 3). However, some agent was also observed (0.16%), as well as a small amount of the diesters (Figure 3). The ^{19}F NMR spectrum of this sample was most conclusive (Table 4 and Figure 4). The alkyl methylphosphonofluoridates represented the major fluorine-containing compounds in the sample (83.2%). Small amounts of F^-/HF and PF_6^- were also observed.

On the other hand, when liquid Sample 26006-1A was acidified to pH 4.5 and extracted with CH_2Cl_2, only PF_6^- was detected by ^{19}F NMR. The ^{31}P spectrum showed the sample contained mainly phosphorus acids and some diesters (Table 3). Qualitatively, the CH_2Cl_2 extract appeared to have less total dissolved ^{31}P compounds than did the chloroform extract, above.

4.2.2 Polymer Phase Sample.

A portion of the polymer sample was dissolved in CH_2Cl_2 (13 wt % polymer) and the resulting solution characterized by ^{19}F NMR spectroscopy (Table 4). The spectrum showed a large resonance for F^-/HF and smaller resonances for PF_6^- and possibly fluorophosphoric acid, with no agent observed. The ^{31}P spectrum showed resonances for methylphosphonic acid and various alkyl methylphosphonic acids. No diesters could be observed, possibly because of the broadness of the resonances in the spectrum.

4.3 Discussion.

The results are based on confirming whether or not agent is present in the chloroform extract as claimed by the original GC analyses, and if so, whether the agent was present in the original caustic solution or reformed during the neutralization and extraction. The first item to notice is that agent is clearly discernible in the chloroform extract. All three methods confirm the original GC results that showed agent present in the chloroform extract of the pH 4 solutions. However, it appears that the agent detected in the chloroform did not come from the original solution in the holding tank. First, the spike of GD added to the caustic solution was not detected, indicating the caustic solution retains its capacity to hydrolyze phosphonofluoridates rapidly. Second, some fluorination reactions clearly are occurring at the lower pH that could produce agent. Given the detectability of the NMR, it is unclear whether the formation of agent occurs in the neutral aqueous solution or whether the reaction occurs in the chloroform between the fluoride and the organophosphorus esters extracted into the chloroform. Finally, the ^{19}F NMR spectrum of a chloroform extract of the pH 13 caustic solution showed no evidence for P-F bond formation. This suggests that even if the formation of agent occurs in the chloroform, the lower pH enhances the reformation of agent, either by chemical reaction or by allowing more organophosphorus and fluoride to be extracted into the chloroform. The absence of

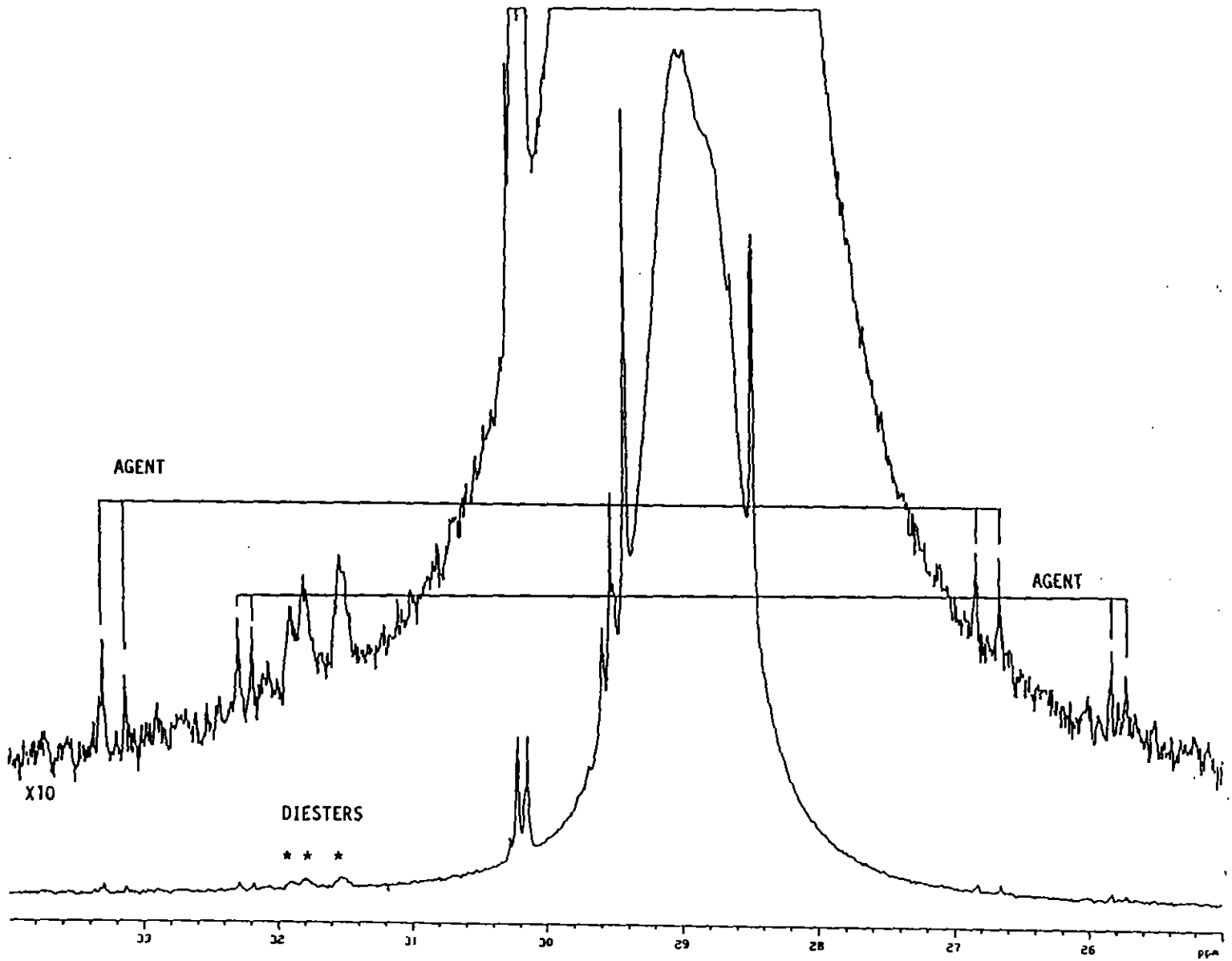


Figure 3. ^{31}P NMR of Sample No. 26006-1B, pH 4.5, $CHCl_3$ Extract

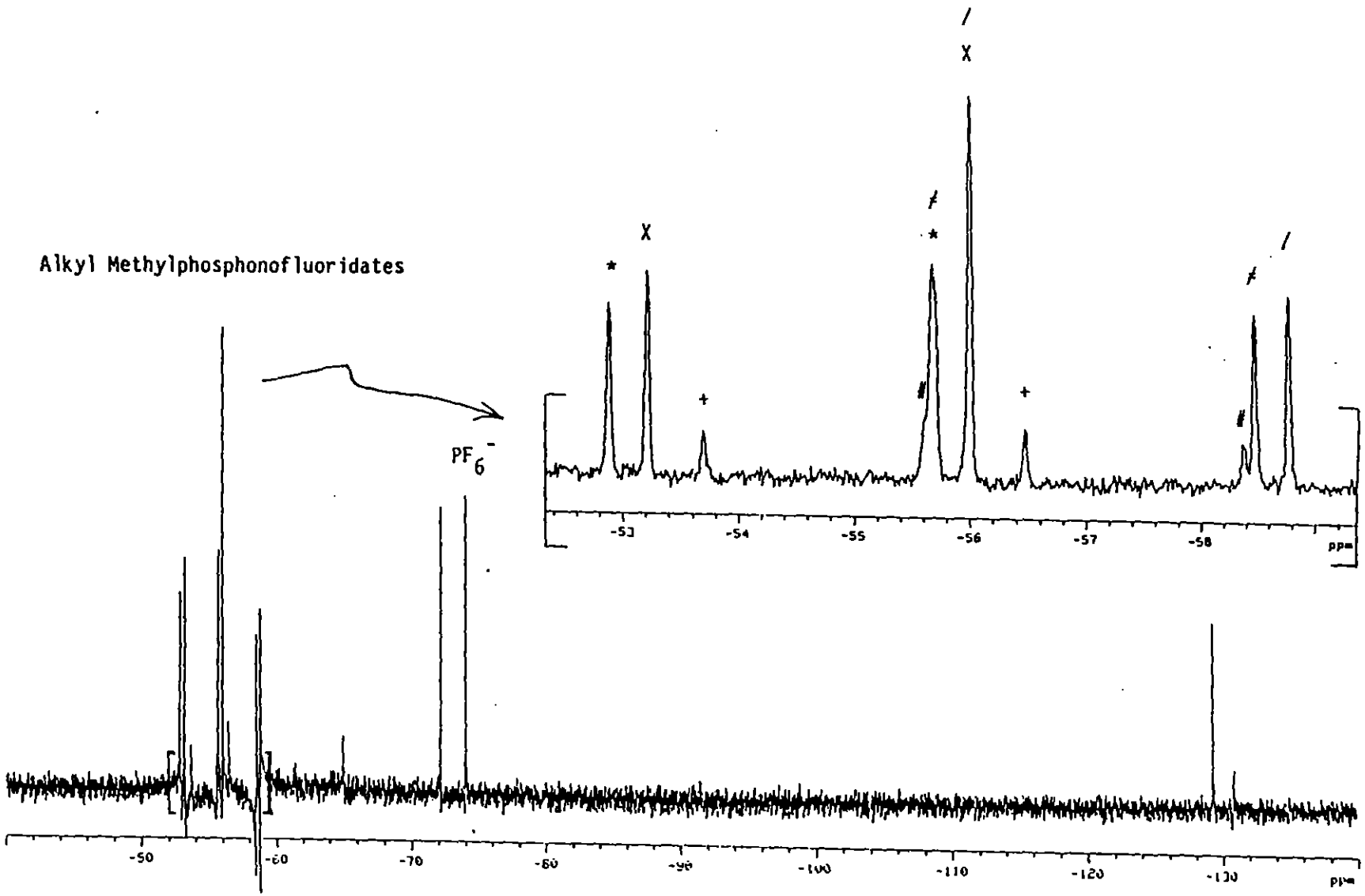


Figure 4. ^{19}F NMR Spectrum of Sample No. 26006-1A, pH 4.5, $CHCl_3$ Extract

agent in the methylene chloride extract also suggests that the agent may be reforming in the chloroform rather than being present in the pH 4.5 aqueous solution.

5. SUMMARY DISCUSSION

The results from GC, GS/MS, and NMR are all consistent with the results of Barrett and co-workers[3] at Southern Research Institute, who found agent even in the chloroform extract from the caustic aqueous solutions. An agent spike rapidly hydrolyzing implies that the agent found in the chloroform extract from the caustic forms in the chloroform.

As part of the assessment of the possibility of G agent persisting in caustic solution, we have examined the chemistry of organophosphorus esters to see if G agents could reform in the presence of base.

It has been shown that fluoride ion may act as a nucleophile for substitution reactions with organophosphorus esters.[6] However, the specific issue is whether fluoride ion can react with a phosphonate monoester such as O-isopropyl methylphosphonic acid (IMPA) to reform the O-isopropyl methylphosphonofluoridate. Griest and Martin[7] specifically addressed this question searching for a way to convert phosphate diesters to phosphorofluoridates. These authors concluded that direct conversion from the phosphate diester to the phosphorofluoridate was difficult if not impossible. Instead, Griest and Martin opted for a sequential method in which phosphate diester reacts with a dialkylcarbodiimide to form a triester that is then converted to a phosphorofluoridate. This is consistent with the view that fluoride ion acts as a nucleophile with fully substituted esters, but the back reaction with the phosphonic acid salt is unlikely. Thus, one would be surprised to see reaction between fluoride and IMPA to form sarin in a caustic solution of IMPA and fluoride. Because the dialkyl methylphosphonates are present in the caustic solutions, fluorination of these compounds is probably the mechanism of G agent reformation in the holding tank samples.

6. CONCLUSIONS

G agent is present in a chloroform extract of the neutralized aqueous solution of decontaminated G agents. The agent in the chloroform likely results from reformation of G agent either in the chloroform or in the neutralized aqueous solutions. Fluorination reactions are detected by NMR spectroscopy in the neutralized aqueous solution. Similar ambiguous results were obtained in the 1970's at CRDEC and Southern Research Institute (Birmingham, AL) when performing analyses of brines from demilitarized agent. An analytical procedure based on the use of methylene chloride for extraction directly from the caustic decontaminating solutions was recommended to preclude anomalous results for G agents. This method recommended by these earlier workers should be used for analyses in lieu of chloroform extraction from neutralized acidified solutions.

Blank

LITERATURE CITED

1. Mabex, W., and Mill, T., "Critical Review of Hydrolysis of Organic Compounds in Water under Environmental Conditions," J. Phys. Chem Ref Data Vol. 7, pp 383-415 (1978).

2. Durst, H.D., Sarver, E.W., Yurow, H.W., Beaudry, W.T., D'Eramo, P.A., Jackson, D.M., Salem, H., Samuel, J.B., Szafraniec, L.L., Ward, F.P., and Ward, J.R., Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD 02 and COMAR 10,31,02,16-1, CRDEC-TR-009, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November 1988, UNCLASSIFIED Report.

3. Barrett, W.J., Dismukes, E.B., Miller, H.C., and Dickson, W.R., Investigation of Contaminants from C-Agent Demilitarization Plants and Determination of Effects on Real Time C Agent Detection Systems, ED-CR-76041, Edgewood Arsenal, Edgewood, MD, December 1975, UNCLASSIFIED Report (AD B008 676L).

4. Epstein, J., Davis, G.T., Demek, M.M., Eng, L., Gorrell, J.D., Pistritto, J.V., Jones, J.T., Schiff, L.J., Richmond, J.A., Sarver, E.W., Block, F., Sommer, H.Z., and Daasch, L.W., On the Mechanism of GB Formation in the Spray Drying of GB Decontaminated Brine Solutions, EC-TR-76009, Edgewood Arsenal, Edgewood, MD, November 1975, UNCLASSIFIED Report (AD A015 427L).

5. Fisher, T.L., Steger, R.J., Parker, G.A., and Sass, S., Gas Chromatographic Methods for the Analysis of Trace Quantities of GB and Associated Compounds (Demilitarization Effluent, Brine, Dried Salts, Munition Exudates), EM-TR-76080, Edgewood Arsenal, Edgewood, MD, September 1976, UNCLASSIFIED Report (AD B015 464L).

6. Cox, R., and Ramsey, B., "Mechanisms of Nucleophilic Substitution in Phosphate Esters," Chemical Reviews Vol. 64, pp 317-352 (1964).

7. Griest, W.H., and Martin, T.W., "Stimulated Sequential Dehydroxy - Fluorination: A Safe, Convenient Method for Gas Chromatographic Analyses of Phosphate Diesters with Possible Application to Hydrolysates of Organophosphorus Pesticides and Nerve Agents," J. Chromatography Vol. 192, pp 173-184 (1980).

Comments on report 8/4/94
by Steve Kimball

1- the agent being analyzed are never mentioned. a slip of the tongue on page 16 indicates that the agents were a product of a binary weapon type experiment. In this case the agents are neither GB or GD.

2- decon mixture

112 Kg	agent	(≈ 30 gal)
273 Kg	NaOH	(600 lbs)
?	water	
Total volume	300 gal	

I think we use a little more decon than this

3- GC/FPD analysis

basic conditions

LOD for 1st extration (.5 ml $CHCl_3$ 1 ml sample) 1 ppm.

LOD for 2nd extration (.5 ml $CHCl_3$ 2.5 ml sample) .4 ppm

neutralized condition

LOD for Neut. (3 ml $CHCl_3$ 150 ml sample) .04 ppm

note this is probably a little off because they do not specify how much acid was added to neutralize the sample LOD in range .04 ± .1 if dilution in acid considered

neutralization ~~probably~~ - may increase sensitivity of analysis by improving extraction efficiency (partitioning coefficie
- salting out effect
- agent forced into acid (organic) form instead of basic (ionic salt) form

5 - GC/MS analysis

agent detected in all samples except one

table 1 appears to have several typo's

- all Table on next page 1 copy 1 for comments

2 - NMR data

- not quantitative
- simple test with 6D showed no regeneration
- stretching hard to wave hands & give explanation of "maybe could ha

Comment 5 Cont.

TABLE 1
Agent Concentrations Observed in Chamber Sample Extracts by GC/MS

Sample	Sample pH Before Extraction	Extraction Solvent	Extraction Ratio	Agent, ppb[a]	
				Extract[b]	Chamber Sample
26323-A (liquid)	>13	$CHCl_3$	2:1	<200	<100
26006-1B (liquid)	>13	$CHCl_3$	5:1	500	100
26006-1C (liquid)	>13	$CHCl_3$	5:1	215	43
26006-1A[c] (liquid)	5	$CHCl_3$	50:1	21,500	430
26006-1B[c] (liquid)	5	$CHCl_3$	50:1	46,500	930
26006-1C[c]	5	$CHCl_3$	50:1	4,000	80
26006-1E (polymer)	--	CH_2Cl_2	5.3:1	<200	<40

[a] Does not include the more volatile agent which is not detected because it coelutes with 1-methyl-2-pyrrolidinone. The more volatile agent is probably also present in concentrations approximately equal to those listed above.

[b] Detection limit of 200 ppb.

[c] Extraction done by Analytical Systems Group.

potential typo's

- samples 4 & 6 seem to be switched
- samples 4, 5, & seem too high by a factor of 10
  if results are divided by 10 then you get numbers consistant with samples 1,

F. Brimhall interpretation:

- The agent was in the waste sample all the time, it was not regenerated by neutralization and extraction with chloroform, i.e. decanta was not complete
- The gc/ms data ~~the~~ support this conclusion, it shows agent in all samples but one, and when sensitivity is by extraction ratio
- The reason agent seems to appear when neutralization is done is because they changed the extraction ratio's and improve the sensitivity of their analysis by a factor of 5 to 10. neutralization might also improve extraction efficiency.

5. No support is shown for their recom. to use methylene chloride for extraction. a reference to 30 year old work. the one sample they used CH_2Cl_2 for was a waste from a sample of plastic (water doesn't extract agent fro plastic with good efficiency. I'd guess < 10%) ther I didn't expect them to find any agent.

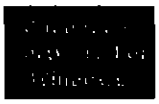
CambridgeSoft ChemFinder.Com ChemACX.Com ChemStore.Com ChemClub.Com ChemNews.Com

ChemFinder.Com

Internet Searching and Information

Go To StoreFronts:

Databases
Reagents
ChemACX Net
ChemACX Pro
Information
ChemIndex
Std Reactions
ChemRXN Std


Enter a chemical name, CAS Number, molecular formula, or molecular weight

ChemFinder
Instructions
About
User Agreement
Indexed Sites
Add URL
Glossary
Typos Quiz
Awards
FAQs
Feedback

Search

Or choose: Advanced Query with Plug-In or Old interface

Purchase a chemical on ChemACX.Com, and get a free subscription
to the ChemACX Pro chemical supplier database, with over 200
catalogs on-line.

Download
Free
Applications
Plugins

A paper describing the ChemFinder WebServer was published in *Chimia* 11/98. A copy is available.

Subscriptions
Information

Individual access to ChemFinder.com is provided as a free of charge service to the scientific community. Access from corporations, academic institutions and government organizations is charged on an annual enterprise subscription basis Please contact CambridgeSoft sales for enterprise subscriptions

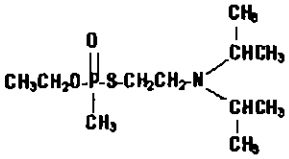
ChemDraw Plugin Authorized Server

CambridgeSoft
ChemFinder.Com
ChemStore.Com
ChemClub.Com

CambridgeSoft ChemFinder.Com ChemACX.Com ChemStore.Com ChemClub.Com ChemNews.Com

Tel: 800 315-7300 / 617 588-9300 **Fax:** 617 588-9390 **Email:**
chemfinderwebserver@camsoft.com
CambridgeSoft, 100 CambridgePark Drive, Cambridge, MA 02140 USA

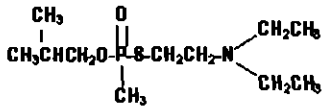
Chemistry of VX



VX has the chemical name methylphosphonothioic acid, *S*-[2-[bis(1-methylethyl)amino]ethyl] *O*-ethyl ester, and has the molecular formula $C_{11}H_{26}NO_2PS$ and formula weight 267.37. Its Chemical Abstracts Service registry number is 50782-69-9.

General Information

The phosphorylthiocholine class of compounds was discovered independently by Ranaji Goshem of ICI and by Lars-Erik Tammelin of the Swedish Institute of Defense Research in 1952. Shortly thereafter, the U.S. Army began a systematic investigation of this class of compounds at Edgewood Arsenal; as a result, VX was developed and stockpiled by the United States.[1] A closely related compound referred to as V gas was manufactured and stockpiled by the Soviet Union. VX is a colorless and odorless liquid.

V gas: 

Reference:

1. Antonov, N., *Chemical Weapons at the Turn of the Century*, LN 72-96, p. 32.

Back to top of this page Back to CW agent list

Physical Properties of VX

Data taken from from Franke, S., *Manual of Military Chemistry, Volume 1. Chemistry of Chemical Warfare Agents*, Deutscher Militärverlag: Berlin (East), 1967. Translated from German by U.S. Department of Commerce, National Bureau of Standards, Institute for Applied Technology, NTIS no. AD-849 866, pp. 247, 252 unless otherwise noted.

REVIEW OF INFORMATION/INFORMATION MATERIALS PA099-363

1 AUTHOR/COTR Extension Office Symbol
C.T. Davis J.B. Connell
F. Block J. Epstein

2. MATERIAL CLASSIFICATION
(Circle one): (UNCL) CONF SECRET
Distribution Limited

3. TYPE OF MATERIAL.
X Technical Report __Contractor Report
__Technical Note __Special Publication
__Oral Presentation __Abstract
__Poster Session __Other

4. FUNDING CATEGORY. (Circle one)
6.1 6.2 6.3. 6.4
6.5 Customer Other
(If customer, please identify)

5. TITLE. Edgewood Arsenal Technical Report EC-TR-76101
Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components

6. TYPE OF RELEASE.

X UNLIMITED DISTRIBUTION. Statement A (Public Release)
__ LIMITED DISTRIBUTION. Select statement below (check one only) and give applicable reason (see chart on page 4 of this form)
__ B - U.S. Government agencies only
__ C - U.S. Government agencies and their contractors only
__ D - DoD and U.S. DoD contractors only
__ E - DoD Components only
__ F - Further dissemination only as directed by Cdr, Chemical and Biological Defense Command (CBDCOM) or his designee.
__ X - U.S. Government agencies and private individuals or enterprises eligible to obtain export-controlled technical data

REASON: High Chemical Agent Rule Repository

__ Classified Material

Security Classification Authority, CLASSIFIED BY:_____

Declassification or Downgrading Instructions, DECLASSIFY ON:_____
DOWNGRADE ON:_____

7. Attached will____will not____be presented to foreign nationals or presented at a symposium where foreign nationals or foreign representatives will be present. (If answer is "will" or "unknown", contact the Counterintelligence Office (Foreign Disclosure) for assistance) (For Limited Distribution Only)

8. Name and address of periodical (If for journal publication):

_____

_____

_____Refereed _____Non refereed

9 Forum:_____

Title. _____

Location _____

Date _____

DoD sponsored: ___Yes ___ No

10. Attached has____has not____been coordinated with contractor. Name and address of contractor:

_____

_____

_____

11. Invention/work described herein has___ has not____been forwarded to Office of the Chief Counsel, CBDCOM.

Name of Inventor:_____

Organization _____

File Number of Invention _____

12. Portion of attached was __ was not__ extracted from copyrighted source

Source Documentation: _____

Permission granted by _____

(Correspondence Attached)

13. APPROVAL RECOMMENDED:

a. Technical Merit

b. Security Classification and Markings Included

c. Data Exchange Agreements/ Memo of Understanding

d. Proper Distribution Markings

e. Patentability /Inventions

f. Contractor Imposed Limited Rights (Proprietary)

g. Confidentiality of Any Contractor or Customer Data

h. News Media/Public Release

i. Required Caveats for Open Literature Publication

j. Operations Security

In reviewing the attached information material, I have considered the above areas and recommend approval:

Team Leader/Division/Office Chief — Date: 25 Jan 99 — Extension: 5-1895

14. SECURITY REVIEW:

✓ Approved ___Disapproved ___See Comments

Counterintelligence Office Reviewer — Date: 4 May 99 — Extension: 3579

15. MILITARILY CRITICAL TECHNOLOGY LIST (MCTL):

___Approved ___Disapproved ___See Comments

MCTL Reviewer — Date — Extension

16. FOREIGN INTELLIGENCE (FI) REVIEW:

✓ Approved ___Disapproved ___See Comments

FI Office Reviewer — Date: 6 May 99 — Extension: 3273

17. INTERNATIONAL PROGRAMS (IP) REVIEW:
(Required for Technical & Special Reports)

TTCP-E - Yes No ... MOU - Yes No Other

IP Office Reviewer — Date — Extension

18. I, the undersigned, am aware of the foreign intelligence interest in open source publications and in the subject matter of the information I have reviewed for OPSEC purposes. I certify that I have sufficient technical expertise in the subject matter of this report/paper and that, to the best of my knowledge, the net benefit of this public release outweighs the potential damage to the essential secrecy of all related CBDCOM, Army, or other government programs of which I am aware.

Recommend release as ___UNCLASSIFIED UNLIMITED.

Director/PM/PD/Office Chief — Date — Extension

Approve release as ___UNCLASSIFIED LIMITED, or ___CLASSIFIED.

19 PUBLIC RELEASE:

✓ APPROVED FOR PUBLIC RELEASE ___FORWARDED FOR HIGHER HEADQUARTERS REVIEW

Chief, Public Affairs Office — Date: 6/21/99 — Extension: X5-5391

20. COMMENTS

AD

EDGEWOOD ARSENAL TECHNICAL REPORT
EC-TR-76101

FUNDAMENTAL STUDIES RELATED TO THE DECONTAMINATION AND DISPOSAL OF GB-FILLED HONEST JOHN WARHEAD COMPONENTS

By

G. T. Davis
F. Block
J. D. Gorrell
J. Epstein

Chemical Laboratory

March 1977

DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
Aberdeen Proving Ground, Maryland 21010

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: EC-TR-76101	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): FUNDAMENTAL STUDIES RELATED TO THE DECONTAMINATION AND DISPOSAL OF GB-FILLED HONEST JOHN WARHEAD COMPONENTS	5. TYPE OF REPORT & PERIOD COVERED: Technical Report December 1974 - January 1976
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): George T. Davis, Frank Block, J. D. Gorrell, J. Epstein	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Commander, Edgewood Arsenal, Attn: SAREA-CL-DC, Aberdeen Proving Ground, MD 21010	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 728012.21
11. CONTROLLING OFFICE NAME AND ADDRESS: Commander, Edgewood Arsenal, Attn: SAREA-TS-R, Aberdeen Proving Ground, MD 21010	12. REPORT DATE: March 1977
	13. NUMBER OF PAGES: 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to US Government agencies only because of test and evaluation; March 1977. Other requests for this document must be referred to Commander, Edgewood Arsenal, Attn: SAREA-TS-R, Aberdeen Proving Ground, Maryland 21010.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

GB	Henry's law	Rate constants	Scrubbers
Disposal	Decontamination	Hydrogen evolution	Vapor pressure
Kinetics	Dichloromethane	Activity coefficients	Sodium sulfate
Raoult's law	Monoethanolamine	Honest John warhead	Sodium hydrogen
Salt effects	Heat of reaction	Partition coefficients	Sodium chloride
			Sodium carbonate

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Investigations related to decontamination and scrubbing of GB in disposal of Honest John warhead components are reported. Calculations are given for expected rates and heats of reactions with aqueous sodium carbonate solutions. Experimental values are reported for rates of reaction of GB with 10% sodium carbonate solutions and 5% sodium hydroxide scrubber solutions. Rates of hydrogen evolution from aluminum bomblet material in contact with sodium carbonate solutions are reported. Vapor pressures of GB in aqueous solution and in aqueous salt solutions were determined. Partition coefficients for methylene chloride-water solutions of GB were determined. Calculated activity coefficients and salting coefficients were used to analyze and compare data. A literature survey of properties of monoethanolamine related to its possible use as a scrubber for GB is summarized in the appendix.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PREFACE

The work described herein was conducted under Project 728012.21, Demil/Disposal, Honest John Warhead Investigations. Work was carried out from December 1974 to January 1976. Experimental data are contained in notebooks MN 2709, MN 2693.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

The information in this document has not been cleared for release to the general public.

CONTENTS

LIST OF TABLES

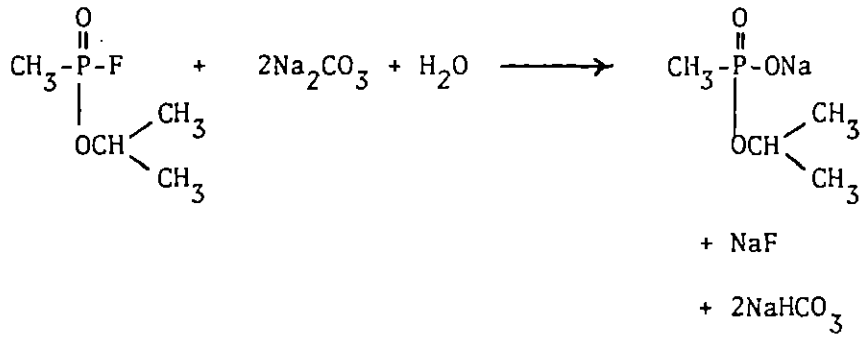
FUNDAMENTAL STUDIES RELATED TO THE DECONTAMINATION AND DISPOSAL OF GB-FILLED HONEST JOHN WARHEAD COMPONENTS

I. INTRODUCTION.

Initially, it was proposed to decontaminate Honest John Bomblets by using 10% aqueous sodium carbonate instead of aqueous sodium hydroxide solutions. This choice was made to alleviate excessive production of hydrogen. (The Honest John components are composed of aluminum alloys.)

Accordingly, a literature survey was conducted of data relevant to the decontamination of GB by sodium carbonate solutions; a system was proposed for the destruction of GB, and calculations of the rate of destruction of GB in the system were made. The temperature rise was also estimated.

Using excess sodium carbonate, the following equation accounts for the reaction of GB with carbonate solutions:



Stoichiometrically, 2 moles of sodium carbonate are required for every mole of GB. Holding this stoichiometry prevents the evolution of carbon dioxide which might entrain some GB into the atmosphere. To guarantee complete reaction, rapid reaction, and freedom from evolution of carbon dioxide, a substantial excess of sodium carbonate should be used. It was proposed that a 300% excess of 10% sodium carbonate be used to decontaminate the GB. Seven gallons of 10% sodium carbonate solution (5.84 lbs sodium carbonate) represents a 300% excess of required base to completely hydrolyze one pound of GB. The pH in such a decontamination system would remain nearly constant at about 11.3.

The rate of reactions of GB in water is general-base catalyzed.[1] Hence, it is controlled by (1) pH and (2) concentration and nucleophilicity (basicity) of dissolved salts. [A complete pH profile of GB for the hydroxide-hydronium ion catalysis of hydrolysis of GB is available in reference (1).]

The pseudo-first-order rate constant for aqueous decomposition of GB in a basic solution of constant pH, containing the additional nucleophilic ion, A (here, A = carbonate ion) is expressed as follows:

$$k_o = k_2 [OH^-] + k_2' [A].$$

where

k_o = the observed first-order rate constant

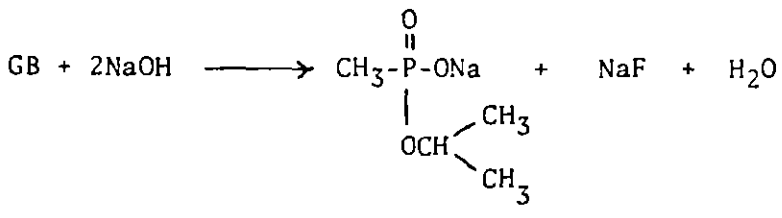
k_2 = the catalytic second-order rate constant for hydroxide

and

k_2' = the catalytic second-order rate constant for A (carbonate ion).

The value of $k_2 = 30\ M^{-1}sec^{-1}$ was obtained from the literature.[2] Similarly, the value of k_2'[3] ($1.25\ M^{-1}sec^{-1}$) has been previously determined. The molarity of 10% sodium carbonate is 0.943, and the molarity of hydroxide ion in such a solution (pH = 11.3) is 2×10^{-3}. Hence, the calculated k_o is $1.24\ sec^{-1}$ at 25°C. Accordingly, the half life may be calculated to be 0.55 sec. (The bulk of catalysis may be seen to accrue from the carbonate ion rather than hydroxide ion by inspection of the two terms during a calculation of the rate constant.) This result means that after 5.5 seconds (10 half lives) only 0.001 lb of GB (from an initial one pound) should remain. In 16.5 seconds (30 half lives) only about 0.4 microgram of GB should remain. Unfortunately, this theoretical result was not realized (vide infra) in the experimental studies that were undertaken later. Upon use of this system, care should be taken that the carbonate does not undergo undue prolonged exposure to the air, resulting in the uptake of carbon dioxide to produce bicarbonate instead of carbonate. The bicarbonate ion would be much less effective than carbonate in the hydrolysis of GB, and it would liberate carbon dioxide upon reaction, which would entrain GB into the atmosphere.

After the system was proposed, it was important to establish that no excessive heat would arise from reaction of one pound of GB with seven gallons of 10% sodium carbonate. The heat of reaction (1) was required. The heat of the following reaction was known[4] to be $\Delta H = -44.4$ kcal/mole:



Since values for ΔH_f (heats of formation) of sodium bicarbonate, sodium carbonate, water, and sodium hydroxide may be obtained,[5] Hess's law of heat summations may be used to obtain the value of ΔH for equation (1). That value is -21.98 kcal/mole (exothermic).

Values for the specific heat of sodium carbonate solutions were available.[6] Interpolation for the molarity (0.943) for a 10% sodium carbonate solution gave a specific heat of 0.947 cal $gm^{-1}deg^{-1}$. This yielded a temperature rise of 2.58°C for the reaction of GB with a 300% excess of 10% sodium carbonate.

Other problems faced with the system were evolution of hydrogen and scrubbing of effluent gases during chemical disposal operations. Experimental studies of hydrogen evolution rates were conducted on actual bomblet material and compared with earlier[7] data. Rates for sodium carbonate destruction of GB were obtained. A rate minimum was established for actual 5% sodium hydroxide scrubber material obtained during the process of "aging" in effluent gases of a pilot run. A literature search considered the possible use of 2-aminoethanol, commonly called monoethanolamine as a scrubber material for GB in the effluents from disposal operations (in which large amounts of carbon dioxide are evolved). In order to estimate the equilibrium quantities of GB swept out of a bubbler under determined steady state or instantaneous concentrations of aqueous GB in salt solutions, the aqueous partial vapor pressures of GB were determined in dilute aqueous solution and in concentrations of model salts.

II. EXPERIMENTAL METHODS.

A. Measurements of Rate of Hydrogen Evolution from Aqueous Sodium Carbonate Solutions.

These experiments were performed at ambient temperature. Each bomblet was found to have the surface area, 190.4 sq. in. One-eighth (or one-sixteenth) of a bomblet was suspended by a nylon string into a stirred solution (6.6 liters) of the appropriate concentration of sodium carbonate solution. The solution, in a large vacuum dessicator was magnetically stirred. The vacuum outlet of the dessicator led to a gas buret containing water as the collection fluid with an attached leveling bulb. At regular time intervals, the volume of hydrogen evolved was measured. Barometric pressure was recorded. Plots of milliliters of hydrogen evolved versus time gave good zero-order (linear) graphs with only a very slight tendency for the reaction rate to increase with time. Reaction is accompanied by an accumulation of surface coating of the black metaaluminate which does not seem to retard the reaction, but in some fashion may facilitate hydrogen desorption.

B. Measurement of Rate of Destruction of GB by Aqueous 10% Sodium Carbonate Solutions.

Reactions were conducted at ambient (approximately 25°C) temperature. A solution of 100 ml of 10,000 ppm GB was mixed rapidly with 100 ml of 20% sodium carbonate in the presence of an aluminum foil square (0.6-in X 0.6-in), and shaken. The initial time was recorded on mixing (1 to 2 sec), and subsequent times were recorded at regular intervals with a stop watch. Five-ml aliquots were withdrawn rapidly by a syringe with a stop, and ejected rapidly into 5 ml of dichlormethane, usually called methylene chloride, for extraction. Upon ejection, the aqueous solution was immediately extracted (2 to 3 sec). It was verified that essentially all GB could be recovered by shaking a methylene chloride solution over such a time period (by shaking 10 seconds, 95-99% of GB was recovered); the methylene chloride layer was separated and

run over a pinch of anhydrous sodium sulfate (for drying) prior to analysis. Analyses were conducted by gas-liquid chromatography (glc) with flame photometric detector and phosphorus filter. One microliter ($\mu\ell$) (or 0.1 $\mu\ell$) samples were injected onto a glass 6-ft × ¼-in 10% QF-1 on 60/80 Gas chrom Q or on 60/70 Anakrom SD (the latter is the better packing) column. The inlet block was at 240°C, detector 140°C, and nitrogen carrier gas was 50 cc/min at 40 psig. The column was held for 1 minute at 100°C, then programmed 100-160°C at 30°C/min. Kinetic results were computer-analyzed.

C. Measurement of Rate of Destruction of GB by Aqueous Sodium Hydroxide (Sump Samples from Scrubbers) Solutions.

Reactions were thermostatted at 13°C. To 100 ml of sump sample was added 0.5 ml of GB. After mixing (2-3 sec), sampling and analysis was conducted similarly to procedure B except that 50-$\mu\ell$ injections of the final extracts were employed. With the interferences present, the GB could be detected readily at 0.006 ppm with a 50-$\mu\ell$ injection. As these reactions were too fast to follow, a 1:10 dilution of the sump samples was mixed with 0.1 ml of GB (1000 ppm initial GB), and runs were conducted at 10°C in the manner described above. With 50-$\mu\ell$ injection, 1.4×10^{-3} ppm of GB would have been readily detected. Again the reactions were too fast to follow.

D. Measurement of Partial Vapor Pressure of GB over Aqueous Solution and over Aqueous Salt Solutions.

Vapor pressure measurements were accomplished by determination of the GB gas concentration in thermostatted flasks at 25.0°C. The flasks were specially prepared from 1000-ml volumetric flasks with silanized surfaces.* A side arm extended downward, containing a mercury seal* over a rubber septum. This system minimized GB vapor absorption by glass walls, and by rubber surfaces. Gastight syringes with silanized surfaces and gas-sampling valves were utilized. It was verified that accurate calibration could be accomplished with liquid standards. Analysis was by vapor phase chromatography employing a flame photometric detector with phosphorus filter. Temperature programming was utilized with computer integration of peaks. Typical conditions were: 6-ft × ¼-in 10% QF-1 on 60/70 Anakrom SD, helium flow 50 ml/min. The column was programmed, after 1-minute delay at 120°C, from 120-240°C at 20°/min. Injection block was 200°C, and detector was 240°C. Calibrations were accomplished within one decade of the measured concentration owing to small nonlinearity of response (4% nonlinearity per decade at the higher loads of sample). Equilibrations required greater than 30 minutes, typically of the order of 1 hour. This limited the ability to go to GB concentrations much larger than those employed. For example, 10,000 ppm solutions of GB underwent autocatalytic hydrolysis at a rate too fast to permit equilibration. For gas analysis, 1.00-cc or 0.100-cc injections were utilized.

E. Measurement of Partition Coefficients of GB Between Aqueous or Aqueous Salt Solutions and Methylene Chloride.

Measurements were conducted at ambient (26+1°C) temperature. Following double extraction, a single phase was analyzed. The aqueous phase from the first partitioning

*The authors are grateful to Mr. J. Pistritto for suggestion of silanization to overcome the glass adsorption which was encountered. Likewise, we are grateful to Dr. J. R. Sowa for suggestion of a mercury seal to overcome the rubber absorption which was encountered.

(1:1 volume-to-volume) was reextracted with an equal volume of methylene chloride. After analysis of this phase, the following formula was applied (for 1:1 extractions); a more general formula is, however, derivable.

$$K = \frac{\frac{Ci_A}{C_{o2}} - 2 \pm \sqrt{\left(\frac{Ci_A}{C_{o2}}\right)^2 - 4\left(\frac{Ci_A}{C_{o2}}\right)}}{2}$$

where

Ci_A = initial concentration of GB if totally in aqueous phase, and

C_{o2} = concentration of GB in second organic phase.

This formula has the advantage of needing analysis of only a single phase, which tends to reduce experimental error. Furthermore, concentration *ratios* are employed rather than differences. The only disadvantage of the formula is that it is double-valued rather than single-valued. If doubt exists as to which value must be selected, analysis of the first organic phase must supplement analysis of the second organic phase. Then, a choice between the two possible values can be made.

III. RESULTS.

Pseudo-first-order rate constants were determined for two experiments in which 5000 ppm of GB was allowed to react with 10% sodium carbonate in the presence of aluminum foil with a surface area equivalent to that of bomblet material in the proposed decontamination system. At ambient temperature, the mean value of k_o (pseudo-first-order rate coefficient was 0.0824 ± 0.0050 sec^{-1}, and the mean value of the half life was 8.45 ± 0.51 sec.

Studies on the rates of hydrogen evolution from aluminum alloy bomblet material are presented in table 1. Values for the kinetic coefficient are given in $ml/in^2/hr$. Kinetics are pseudo-zero-order since the aluminum surface area remains essentially constant during the course of reaction. Accumulation of a surface coating of metaaluminate during the reactions *did not retard* the reaction, but very slight *accelerations* with time were observed.

Sump samples from scrubbers of gases during disposal operations were received for evaluation of their kinetic efficacy before and after "aging" during the scrubbing process. Originally, the scrubber solutions were composed of 5% aqueous sodium hydroxide solutions. Attempts to obtain rate constants at 13°C for reactions of the undiluted sump samples with 5000 ppm GB were unsuccessful owing to the extreme rapidity of reaction. After 13-sec reaction time, <0.006 ppm GB remained from an initial concentration of 5000 ppm (99.9999% reaction). Reactions of 1000 ppm GB with 1:10 dilutions of the sump solutions were likewise too fast to follow. Nevertheless, a *minimum* rate constant could be calculated as well as a *maximum* half life. Results are summarized in table 2.

Table 1. Rates of Hydrogen Evolution from Honest John Bomblet Material Suspended in Stirred Aqueous Sodium Carbonate Solutions

% Sodium carbonate	Amount of bomblet*	pH	Temperature	Barometric pressure	k
			°C	mm Hg	$ml/in^2/hr$
10	1/8	11.24	27.0	762.3	11.7±0.2
5	1/8	11.14-11.19	26.0	762.0	10.4±0.6
1	1/8	11.18-11.17	25.0	757.6	7.32±0.48
0.1	1/8	11.16-10.69	24.5-27.0	759.6	2.65±0.35
10	1/16	11.16-11.14	27.0	762.4	12.48±1.08

*Each bomblet has a surface area of 190 in^2.

Table 2. Analyses and Rate Comparisons for Sump (Scrubber) Material Withdrawn at Rocky Mountain Arsenal During Pilot Scrubber Operations

Sample	Time	Sump temperature	pH*	NaOH* content	Na_2CO_3* content	Half life (10°C) (1:10 dilution)	Calcd half life (10°C) for undiluted sample
	min	°F		mg/ml	mg/ml	sec	sec
1	0	70	12.6	46.1	0.4	<0.82±0.01	<0.082
7	265	52	12.8	38.5	13.9	<0.77±0.05	<0.077

*Analyses by Mr. Paul Davis, Analytical Chemistry Branch.

The partial aqueous vapor pressures of GB in dilute solutions are reported in table 3. The data approximately follow Henry's Law in the concentration region of measurement, but deviate widely (10 times) from Raoult's Law. The *concentration* of GB in the vapor phase was directly measured, and this value was used to calculate (from the ideal gas law) the *partial pressure* of GB in the vapor.

From the values of table 3, an average value for the Henry's Law coefficient of GB was calculated.

Decontamination of GB in the Honest John program, as suggested previously, was to be accomplished by sodium carbonate solutions or sodium hydroxide solutions. Scrubbing of

Table 3. Aqueous Partial Vapor Pressures of GB at 25.0°C

Concentration of GB	Partial vapor pressure* of GB	Ideal partial vapor pressure calculated from Raoult's law
ppm	mm Hg	mm Hg
2160	$1.06 \pm 0.03 \times 10^{-2}$	7.92×10^{-4}
432	$2.29 \pm 0.09 \times 10^{-3}$	1.59×10^{-4}
216	$1.16 \pm 0.03 \times 10^{-3}$	0.792×10^{-4}

*Mean Henry's Law coefficient = 0.727 mm/mole/liter.

effluent gases in salt disposal was to be accomplished with sodium hydroxide or sodium carbonate solutions. It was desirable to be able to predict qualitatively the vapor pressure of GB over a steady state or instantaneous concentration of GB in the salt solutions. Because of the previously demonstrated high reactivity of GB with 10% sodium carbonate, or 5-10% sodium hydroxide, it is not possible to obtain the vapor pressure over solutions of these salts. However, model salts were chosen for qualitative prediction of the effect of salt on vapor pressure. Sodium chloride (a 1:1 electrolyte) was chosen as the model for sodium hydroxide. Sodium sulfate (a 1:2 electrolyte) was chosen as the model for sodium carbonate. The 1.25 M solutions of sodium chloride correspond closely (in molarity) to 5% solutions of sodium hydroxide. The 1M sodium sulfate solutions correspond closely to 10% sodium carbonate solutions (in molarity). Results for sodium chloride are presented in table 4.

Table 4. Partial Vapor Pressures of GB in Aqueous Sodium Chloride Solutions at 25.0°C

Concentration of GB	Molarity NaCl	Partial vapor pressure GB	Activity coefficient*
ppm		mm Hg	
2160	1.25	$1.68 \pm 0.06 \times 10^{-2}$	1.50
432	1.25	$3.30 \pm 0.08 \times 10^{-3}$	1.47
216	1.25	$1.48 \pm 0.04 \times 10^{-3}$	1.32
2160	2.50	$2.52 \pm 0.07 \times 10^{-2}$	2.25
432	2.50	$5.5 \pm 0.5 \times 10^{-3}$	2.46
216	2.50	$3.1 \pm 0.2 \times 10^{-3}$	2.76

*Activity coefficients are calculated relative to a Henry's Law standard state. The standard state would be hypothetical unit concentration *at infinite dilution, i.e.* 1 molar GB at infinite dilution in aqueous solution, having a vapor pressure equal to the Henry's Law coefficient, 0.727 mm. It is also possible to calculate activity coefficients relative to a Raoult's Law standard state.

Results for sodium sulfate are presented in table 5. As is immediately apparent, the equimolar salting effect of sodium sulfate is greater than that of sodium chloride.

Table 5. Partial Vapor Pressures of GB in Aqueous Sodium Sulfate Solutions at 25.0°C

Concentration of GB	Molarity Na_2SO_4	Partial vapor pressure GB	Activity coefficient*
ppm		mm Hg	
2160	0.373	$1.75 \pm 0.04 \times 10^{-2}$	1.54
432	0.373	$3.07 \pm 0.05 \times 10^{-3}$	1.37
216	0.373	$1.67 \pm 0.05 \times 10^{-3}$	1.49
2160	1.000	$3.60 \pm 0.04 \times 10^{-2}$	3.21
432	1.000	$7.09 \pm 0.15 \times 10^{-3}$	3.17
216	1.000	$3.15 \pm 0.09 \times 10^{-3}$	2.81

*Activity coefficients are calculated relative to a Henry's Law standard state. The standard state would be hypothetical unit concentration *at infinite dilution, i.e.* 1 molar GB at infinite dilution in aqueous solution, having a vapor pressure equal to the Henry's Law coefficient, 0.727 mm. It is also possible to calculate activity coefficients relative to a Raoult's Law standard state.

Values for the partition coefficients of GB between the aqueous salt solutions and methylene chloride have also been obtained for comparison with the vapor pressure data. These comparisons are made through the calculated activity coefficients relative to infinitely dilute GB. These results are summarized in table 6.

Table 6. Values of Partition Coefficients* Between Aqueous Salt Solutions and Methylene Chloride for Partitioning of GB at Ambient Temperature (26±1°C).

Salt	Salt molarity	K	Activity coefficient
None	-	15.95±0.03	1.00**
Sodium chloride	1.25	27.60±0.00	1.73
Sodium chloride	2.50	40.07±0.62	2.51
Sodium sulfate	0.373	28.77±0.01	1.80
Sodium sulfate	1.000	64.74±0.18	4.05

*$K = \frac{\text{Organic}}{\text{Aqueous}}$

**Extractions were performed on very dilute (108 ppm) initial concentrations of GB. It is considered that the partitioned aqueous phase in the salt-free extraction is equivalent to the standard state of Henry's Law (infinite dilution). However, the definition is inexact here, since methylene chloride dissolves about 2% into the aqueous phase and some water dissolves into the methylene chloride phase. For this reason, only approximate agreement is to be expected for partition coefficient data and partial pressure data.

IV. DISCUSSION.

As seen from comparison of the predicted half-life (0.55 sec) in the Introduction, and that actually found experimentally (8.45 sec) in the Results, there is a considerable defect in concentrated-solution reactivity of sodium carbonate and GB with respect to that predicted from dilute solution kinetics. The dilute solution calculation derives most of its reactivity (>94%) from the carbonate ion. We attribute the experimental defect in reactivity (as opposed to the predicted value) to a marked decrease in activity of carbonate ion in these high concentrations, and to substantial formation of carbonate ion pairs of reduced reactivity. The magnitude of these effects must indeed, be great when it is noted from tables 5 and 6 that the activity coefficient of GB is actually *raised* 3 to 4 times in 1 M solutions of a 1:2 electrolyte. Other things being equal, this latter effect should cause an *increase* in reactivity of GB with 10% (~ 1 M) sodium carbonate solutions. Thus, the ion-pairing and ion activity reduction in reactivity of carbonate ion must be of the order of 98-99% loss. At any rate, this lowered reactivity can cause problems in scrubbing efficiency if the gas residency time becomes lower than 80 sec in the scrubber (10 half lives). Certainly, the scrubbing efficiency is too low for gas residency times of the order of 8 sec. (~ 50% reaction before equilibrium vapor emission of GB).

From the data of table 1, a mean value of 12.1 ml/in^2/hr is found for the rate of evolution of hydrogen from an Honest John Bomblet. Previous data from Hildebrand[7] had allowed calculation of a value of 4.8 ml/in^2/hr for a pH of 11.3. Thus, our values are 2.5 times greater than those reported by Hildebrand. Our data show that appreciable quantities of hydrogen will be evolved from one bomblet in one minute of contact (about 38.4 ml). The data of table 1 also show some specific ion evolution of hydrogen by carbonate, though the effect is small. Most of the variation observed can be attributed to pH changes. Furthermore, the first and last entries of table 1 establish the proportionality between rate of hydrogen evolution and aluminum surface area. Hence, the rate law is as follows:

$$\text{Rate} = \frac{d[H_2]}{dt} = k\,[\text{Area}]\,[OH^-] + k_2'\,[\text{Area}][CO_3^=]$$

This reduces to zero-order kinetics when the pH and area of aluminum do not sensibly change.

In table 2, it is seen that the caustic depletion effect from 4 hours' scrubbing with 5% sodium hydroxide solutions is about 15% conversion of hydroxide to carbonate. The effect on kinetic efficiency is negligible. However, one might have concern over use of these scrubbers for a more protracted (e.g., 30 hr) length of time. For example, if all of the hydroxide becomes converted to carbonate, the half life of GB will approach 8 seconds or more instead of the initial half-life of <0.08 seconds. Hence, a literature inquiry was made as to the possible use of monoethanolamine (MEA) as a regenerable scrubber (see the Appendix). It was concluded that MEA would be useful only at elevated temperatures, and that an inadequate data base exists concerning reactivity of GB with MEA.

Previously, Higuchi[8] had measured partial pressures of GB in aqueous solution in the Henry's Law (infinite dilution) region. His measurements were at 30°C, and he expressed doubts over precision and accuracy greater than about 20% owing to hydrolysis of GB during the conduct of the experiments. The data of table 3 were obtained in the absence of appreciable hydrolysis of GB by working in more dilute concentration ranges than those employed by Higuchi. In addition, a "static" system rather than a flow system was employed, enabling multiple sampling to determine that equilibrium was, in fact, extablished. Our results are in excellent accord with Higuchi's data.

Dilute solutions of GB obey Henry's Law (table 3) but not Raoult's Law. Positive deviations (13.4 times the value; Higuchi obtained a value of 13.6 times theoretical at 30°C) from Raoult's Law are observed. An "activity coefficient" of 13.4 is thus obtained for GB in dilute aqueous system relative to pure liquid GB as the standard state. There has been expression of suprise[8] over this result, since GB is considered to be a hygroscopic liquid, and to interact widely with hydrogen bond donors such as water. Higuchi concluded that the effect was due to the extremely high internal pressure (structure-making tendency) of water. However, it is our contention that other factors are involved in comparing a Raoult's Law standard state with a solution in the Henry's Law region which also allows an explanation of a strong positive deviation from Raoult's Law. At the outset, it is only ideal solutions which conform to Raoult's Law. Secondly, in comparing a dilute solution in the Henry's Law region to a Raoult's Law standard state, we are comparing the escaping tendency of a solute from two different media, one medium being the pure substance. For GB, the liquid cohesion forces can be divided into Van der Waal's attractive (or dispersion) forces, and permanent dipolar interactions. Because of the relatively large size of GB (compared to water), the Van der Waal's forces in pure GB will be extremely large [Cf. ref. (9) for a comparison of the relative magnitudes of dispersion forces and dipolar forces]. When GB is dissolved in water, the large dispersion forces around GB are displaced by much weaker dispersive attractions with water, and dipolar and electrostatic hydrogen-bonding forces, but the latter are not likely to compare with the magnitude of dispersive forces in pure GB [Cf. ref (9)]. Hence, it is quite possible that the large activity coefficient of GB in water relative to pure GB is a result mainly of *attractive dispersion forces* in GB which are depleted in water, rather than a result of the great structure-making tendencies of water. At any rate, it should not be surprising that the *combination* of structure-making tendencies within water, and the loss of dispersion forces upon separating GB molecules can lead to a greater escaping tendency of GB from water than from pure liquid GB.

The salting effects of the two model electrolytes as measured by the activity coefficients relative to a Henry's Law standard state (tables 4 to 6) are most certainly the result of specific salt effects as well as ionic strength effects. The ionic strength effect of electrolytes on the activity of a nonelectrolyte has been theoretically explored.[10] One of the formulations proposed is:

$$\log \gamma = k_m \mu$$

Here, γ is the activity coefficient of a neutral molecule. The constant, k_m is a "salting coefficient", and μ is the ionic strength. The equation has been successfully and empirically applied to data with large ionic strengths. The vapor pressure data provides a salting coefficient

of 0.14 for sodium chloride as compared with a value of 0.17 from the partition coefficient data. For sodium sulfate, the vapor pressure data can be used to calculate a salting coefficient of 0.16 as compared with a value of 0.22 from the partition coefficient data. Comparison of the Henry's Law activity coefficients from vapor pressure measurements (tables 4 and 5) with those from partition coefficient measurements (table 6) shows that the two different kinds of data are in qualitative, but not quantitative agreement. Except for the values of 2.5 M sodium chloride, the partitioning activity coefficients have a tendency to be 20-30% larger than the vapor pressure activity coefficients. As noted in the footnote of table 6, only approximate agreement is to be expected between the two kinds of data owing to inexactness in obtaining pure phases in the partition coefficient measurements.

Data from the partition coefficient measurements and vapor pressure measurements have served to establish the magnitude of salting effects on the activity of GB. Hence, the vapor pressure of GB in aqueous 10% sodium carbonate will be about 3 times the value in pure water, while the vapor pressure of GB in aqueous 5% sodium hydroxide will be about 1.5 times the value in pure water. Analytically, the data of the present report can be used to predict salting effects of electrolytes on partition coefficients for extraction of GB.

These studies were made to provide background information to the problem of decontamination of GB filled Honest John warhead components. The data generated indicate that (1) the vapor pressure of GB in scrubber solution expecially Na_2CO_3 can be considerably higher than one would predict from Raoult's Law and (2) the reaction of GB with Na_2CO_3 is, although rapid, considerably less rapid than one would have predicted from extrapolation of data obtained in dilute solution. These two effects should be considered in the design of decontamination equipment and procedures. For example, the scrubber solution cannot contain more than 3 parts per billion of GB if the vapor over the solution is to be less than 0.0003 $\mu g/l$ in GB. The residence time of a gas to be scrubbed by the Na_2CO_3 should consider the time of contact required to reduce the concentration of GB entering the scrubbing solution to below 3 parts per billion.

One can possibly get high rates of reaction with other bases such as trisodium phosphate. A study of the rates of reaction between GB and other basic ions is indicated. Moreover, the data of Higuchi (loc cit) indicate that there are materials which decrease the activity coefficient of GB. Some of these materials (or those extrapolated from his data) might be considered if it is decided that a new look is needed into the problems in decontamination and scrubbing of GB.

LITERATURE CITED

1. Epstein, J. Properties of GB in Water. J. Am. Water Works Assn., *66(1)*, 31-37 (1974).

2. Larsson, L. The Alkaline Hydrolysis of Isopropoxymethylphosphonyl Fluoride (Sarin) and Some Analogues. Acta Chem. Scand. *11*, 1131–1142 (1957).

3. Healy, T. V., Kinetics of the Hydrolysis of GB and GE - Part II. Porton Technical Paper No. 78. November 1948.

4. Neale, E. The Thermochemistry of Organic Phosphorus Compounds. Part III. Porton Technical Paper No. 339. November 1953.

5. Dean, John A., Editor. Lange's Handbook of Chemistry, 11th Edition. McGraw-Hill Book Co., New York, New York. 1973.

6. Handbook of Chemistry and Physics, 37th Edition. Chemical Rubber Publishing Co. Cleveland, OH. 1955.

7. Hildebrand, H. F. Operations Engineering Section, DF: Memorandum for Record to the Chief, Plant Design Section, subj: Experiments on Hydrogen Evolution for TDS. May 13, 1971.

8. Higuchi, T., and Kinkel, A. W. Surface Effects in Detection, edited by J. I. Bergman and A. Dravnieks. Spartan Books, Inc., Washington, DC. MacMillan and Co. Ltd. London (1965). p. 311. An Apparatus for Vapor Pressure Measurement of Slightly Volatile Solutes.

9. Glasstone, S. Textbook of Physical Chemistry, Second Edition. p. 300. D. Van Nostrand Co., New York. 1946.

10. Harned, H. S., and Owen, B. B. The Physical Chemistry of Electrolytic Solutions, 3rd Edition. p 531-540. Reinhold Publishing Corp., New York 1958.

APPENDIX

Literature Survey Pertinent to Application Monoethanolamine as a Scrubber Material for GB

Selected literature references reveal that 2-aminoethanol, commonly called monoethanolamine (MEA) and aqueous solutions of MEA have found extensive international use in removal of carbon dioxide (and other gases such as H_2S) for CO_2 recovery, and CO_2 removal from gases during purification.

Fundamental Data. An early report[1] summarized the available fundamental data on equilibrium solubility and absorption rates by aqueous solutions of MEA. Very recent reviews contain similar information of value in process planning for utilization of MEA as absorbent for carbon dioxide. Tables and data on physical, chemical, and thermal properties of MEA and aqueous solutions are presented, with data on the equilibrium absorption of carbon dioxide, degree of conversion to carbamates, etc.[2] A process review on the use of MEA to remove carbon dioxide from ammonia synthesis gas is available.[3] Data concerning the solubility of carbon dioxide in 5.0 N MEA solution determined between 40°C and 100°C at various partial pressures has been summarized.[4] Differential and integral heats of solution of carbon dioxide in aqueous MEA have been evaluated.[5] Calculation methods for solutions of variable aqueous and carbonation contents have been presented for 65-130°C at levels of 0.07-0.67 moles CO_2/mole MEA and concentrations of 10-20% MEA.

Equations derived from existing laws of nonelectrolyte solutions with the assumption that the basic reaction product is the bicarbonate of MEA have been shown to be in error.[6]

Mechanical and Geometric Effects in Absorption of MEA. The absorption of carbon dioxide by monoethanolamine in the neat state has been shown to be hampered by the viscosity of the liquid and the sticky characteristics of the fluid. The use of mechanical dispersers is advocated to split the liquid into small drops for the formation of a larger active surface.[7] The efficiency of absorption is thus improved.

Further studies of mechanical and geometric effects on the efficiency of absorption of carbon dioxide by MEA solutions have been conducted by a large number of workers. Most of these reports are in the Russian literature, and are not readily accessible. One report[8] appears in the English literature.

Kinetics. A massive number of publications, mostly in the Russian literature, report on the kinetics of absorption of carbon dioxide by MEA. Very complex equations have been developed including physical absorption effects, mass transfer, diffusion, chemical reaction, and equilibria. Among the English references available are 9, 10, 11, 12, 13, 14, and 15.

Reversibility and Regeneration. The reversibility of carbonation and widespread ease of regeneration of MEA from its carbonated solutions has been amply reported upon, especially in the Russian literature.[16-19] Kinetics of desorption have been obtained.[17]

Based upon this reversibility, continuous processes have been described for absorption of carbon dioxide and regeneration of MEA.[20] Some references appear in the Russian and patent literature.

Mechanism of CO_2 Absorption. The absorption of carbon dioxide by MEA involves both physical and chemical processes. One model which has been suggested is that of a physical gas absorption followed by a two-step chemical reaction. Data from the literature followed certain aspects of this model.[21] It has been shown[16] that for molar ratios of CO_2/MEA <0.5, a second-order fast chemical absorption takes place with a stoichiometric coefficient of 2 moles MEA per mole of CO_2. This could correspond to production of (2-hydroxyethyl)ammonium carbonate $(HOCH_2CH_2NH_3^+)_2\ (CO_3^=)$ or (2-hydroxyethyl)ammonium (2-hydroxyethyl)-(carbamate) $(HOCH_2CH_2NH_3^+)\ (HOCH_2CH_2NHCO_2^-)$. When the CO_2/MEA ratio reaches >0.5, the reaction becomes pseudo-first-order, and slow, with an overall kinetic constant depending upon pH (directly proportional to OH concentration). This latter reaction is evidently a catalyzed rearrangement of carbamate to carbonate followed by further carbonation (and hydration) to give the bicarbonate. Further, it is demonstrated[13] that carbon dioxide hydration catalysts could affect the rates of CO_2 absorption by aqueous monoethanolamine. Later[22] it was determined that rapidly formed carbamate reacts slowly to give the bicarbonate. There is, thus, produced a metastable equilibrium pressure of CO_2 with the carbamate which decays slowly to a final equilibrium pressure involving carbamate and bicarbonate. Whymark and Ottaway[23] showed that carbon dioxide reacts with MEA in pyridine to produce (2-hydroxyethyl)ammonium (2-hydroxyethyl)carbamate, a result in agreement with the previous observations.

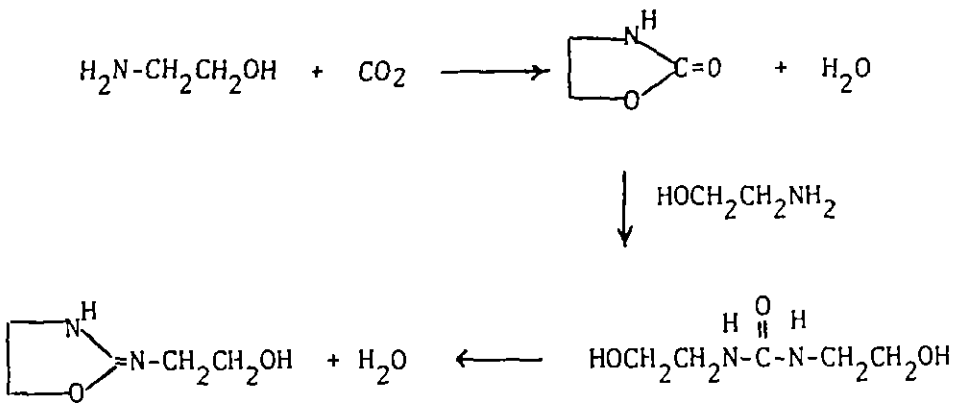
More recently, it has been discovered[24] that the carbonation reactions of MEA produce additional products, including N-(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl)-2-imidazolidinone, and 2-oxazolidinone. It was later reported[25] that 2-oxazolidinone is attacked by MEA to produce the intermediate, *bis*-(2-hydroxyethyl)urea which then cyclizes to 1-(2-hydroxyethyl)-2-oxazolidinone. It should be noted that the more recently isolated products of carbonation of MEA are apt to be formed irreversibly since it is likely that thermal reversal of their formation would be slow.

A scheme accounting for the determined equilibria and some of the products is the following:

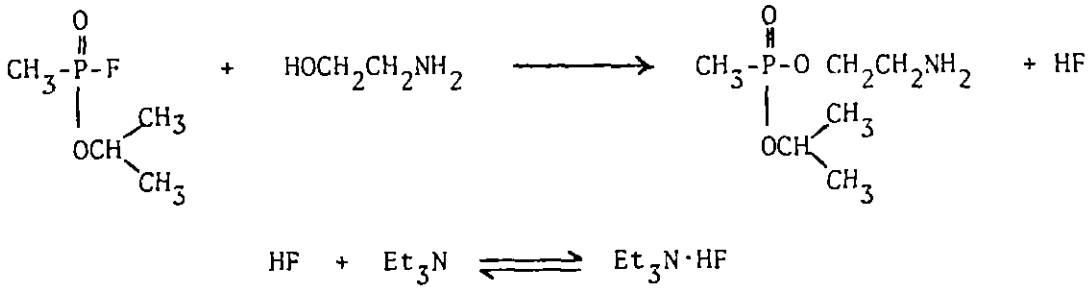
$$2H_2NCH_2CH_2OH + CO_2 \xrightleftharpoons{\text{fast}} (HOCH_2CH_2NH_3^+)\,(HOCH_2CH_2\overset{H}{\underset{|}{N}}\text{-}CO_2^-)$$

$$\Big\downarrow\Big\uparrow \quad CO_2 \quad \text{slow}$$
$$2H_2O$$

$$2\,(HOCH_2CH_2NH_3^+)\,(HCO_3^-)$$



Reaction of MEA with GB (Sarin). Only two studies of the reaction of MEA wi organophosphorus esters related to GB are reported.[26,27] No kinetics have been determined. T reaction of GB with MEA with a 1:1 ratio of reactants in chloroform (with triethylamine prese as a proton acceptor) occurs in the following way:



The authors contend that the reaction is "slow" though no kinetics are presented. React times utilized are of the order of 1 day at the temperature of refluxing chloroform, and 4 d at room temperature. Concentrations of the reactants were 5 M. These results may not be u to forecast the reactivity of neat MEA or aqueous MEA with GB, since a high dielectric const [such as MEA ($\epsilon = 37.7$) and water ($\epsilon = 77.9$)] would favor reaction between these materials opposed to the poor, low dielectric ($\epsilon \cong 5$) of chloroform. Chemical analogy suggests that reaction of GB with neat MEA will be fast since the reactivity of methoxide ion in methanol solvent of comparable dielectric constant ($\epsilon = 26$) to MEA] is quite good ($k_2 = 40.3\ M^{-1}$sec reference 28). Furthermore, the autolysis of MEA to produce $H_3N\text{-}CH_2CH_2O^-$ $H_2N\text{-}CH_2CH_2O^-$ should provide appreciable concentrations of these nucleophilic ions. Howe uptake of CO_2 could suppress formation of the desirable nucleophilic species.

Analytical Methods. Analytical methods have been described for the determinat of the carbon dioxide content of MEA solution.[29,30]

Summary and Conclusions. The use of MEA as a regenerable scrubber for CO_2 is well-documented and studied. Efficiency for removal of CO_2 is high; this is not a particularly desirable trait for the scrubber under consideration. It would be desirable to eliminate absorption of CO_2, if possible, while preserving reactivity capability for GB. The viscosity of neat MEA is high, and inconvenient for a scrubber material. The reactivity of neat MEA or aqueous MEA with GB has not been demonstrated kinetically. "Slow" reactions have been obtained in chloroform. Products consist virtually entirely of the oxy-anion attack.

It is considered that many of the contemplated difficulties with employment of MEA as a scrubber material could be overcome. For example, if the neat material were used at 100°C its propensity for CO_2 absorption could be much-reduced. Its viscosity would also be reduced. Any remaining viscosity problems could be overcome by introducing mechanical turbulence. Conducting the scrubbing action at elevated temperatures would produce higher reactivity for GB, an added bonus.

SELECTED REFERENCES

1. Mason, J. W., and Dodge, B. F. Equilibrium Absorption of Carbon Dioxide by Solutions of the Monethanolamines. Trans. Am. Inst. Chem. Eng., *32*, 27-48 (1936).

2. Strelzoff, S. Carbon Dioxide Removal XIII. Data on Amines and Potassium Carbonate Solutions. Fert. Sci. Technol. Ser., *2*, 253-287 (1974).

3. Jackson, J. M. Carbon Dioxide Removal VI. Monoethanolamine (MEA). Fert. Sci. Technol. Ser., *2*, 183-199 (1974).

4. Lee, J. I., Otto, F. D., and Mather, A. E. Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 5.0 N Monoethanolamine Solution. J. Chem. Eng. Data., *20*, 161-163 (1975).

5. Murzin, V. I., Argunova, V. I., Leites, I. L., Tyurina, L. S. Determination of the Enthalpies of Carbonated Aqueous Solutions of Monoethanolamine and Gas Vapor Mixtures in the Design of Processes of Removing Carbon Dioxide from Gases. C.A., *80*, 31076k (1974).

6. Klyamer, S. D., Shklyar, R. L., Voloshin, V. I., and Tutaeva. Equilibrium Absorption of Hydrogen Sulfide and Carbon Dioxide in Monoethanolamine Solutions. C.A., *81*, 17360n (1974).

7. Koch, R. The Absorption of Carbon Dioxide by Ethanolamines in New Types of Mechanical Absorbers. C.A., *53*, 17367d (1959).

8. Malpani, S. N., and Donnelly, J. K. Identification of a Packed Absorption Column. Can. J. Chem. Eng., *51*, 479-483 (1973).

9. Thomas, W. J. The Absorption of Carbon Dioxide in Aqueous Monoethanolamine in a Laminar Jet. A.I.Ch.E. J. *12(6)*, 1051-1057 (1966).

10. Astarita, G., Marracci, G., and Giora, F. The Influence of Carbonation Ratio and Total Amine Concentration on Carbon Dioxide Absorption in Aqueous Monoethanolamine Solutions. Chem. Eng. Sci., *19*, 95-103 (1964).

11. Goodridge, F. Kinetic Studies in Gas-Liquid Systems. Part 2 - Initial Absorption Rates of Carbon Dioxide in Amine Absorbents. Trans. Faraday Soc., *51*, 1703-1709 (1955).

12. Goodridge, F. Kinetic Studies in Gas-Liquid Systems. Part I - A Diaphragm Method of Following Initial Absorption Rates. Trans. Faraday Soc., *49*, 1324-1332 (1953).

13. Danckwerts, P. V., and McNeil, K. M. The Effects of Catalysis on Rates of Absorption of CO_2 into Aqueous Amine - Potash Solutions. Chem. Eng. Sci., *22*, 925-930 (1967).

14. Clarke, J. K. A. Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times. Ind. Eng. Chem. Fundam., 3, 239-245 (1964).

15. Emmert, R. E., and Pigford, R. L. Gas Absorption Accompanied by Chemical Reaction: A Study of the Absorption of Carbon Dioxide in Aqueous Solutions of Monoethanolamine. A.E.Ch.E. J., *8*, 171-175 (1962).

16. Aksel'rod, Yu., V., Lyubruskina, L. A., and Leites, I. L. Effect of Carbonate-Bicarbonate Equilibrium in Carbonated Monoethanolamine Solutions on Carbon Dioxide Pressure. C.A., *77*, 66875k (1972).

17. Ellis, G. C., Leachman, G. S., *et al.* Rate of Desorption of Carbon Dioxide from Ethanolamines. Proc. Gas. Cond. Conf., 1B-10B (1963).

18. Katsynel, M. B., and Blonskii, S. D. Analytical Factors Describing the Absorption-Desorption Ethanolamine Process in the Production of Carbon Dioxide. C.A., *64*, 13790c (1966).

19. Cherevaiko, V. P., and Shapirov, R. S. Removal of Carbon Dioxide from Inert Gas by Monoethanolamine in Catalytic Reforming Plants. C.A. *61*, 9336g (1964).

20. Viescou, C., and Vec, R. Continuous Removal of Carbon Dioxide from Air. C.A., *76*, 115248y (1972).

21. Brian, P. L. T., and Beaverstock, M. C. Gas Absorption. Accompanied by a Two-Step Chemical Reaction. Chem. Eng. Sci., *20*, 47-56 (1965).

22. Aksel'rod, Yu. V., *et al.* Kinetics of Carbon Absorption by an Aqueous Monoethanolamine Solution. C.A., *73*, 27043k (1970).

23. Whymark, D. W., and Ottaway, J. M. Absorption of Carbon Dioxide in Solutions of Monoethanolamine. Talanta *19(2)*, 209-212 (1972).

24. Bogoslovskii, Yu., *et al.* Analysis and Identification of Reaction Products of Monoethanolamine Formed During the Removal of Carbon Dioxide from Gases. C.A., *80*, 78183h (1974).

25. Yazvikova, N. V., *et al.* Mechanism of the Side Reactions During the Monoethanolamine Separation of Gases from Carbon Dioxide. C.A., *82*, 138867n (1975).

26. Greenhalgh, R., and Weinburger, M. A. The Selective Phosphylation of Ethanolamine. Can. J. of Chem., *45*, 495-500 (1967).

27. Greenhalgh, R., Heggie, R. M., and Weinburger, M.A. Effect of the Structure of Phosphylating Agents on their Reaction with Ethanolamine. an Ambient Nucleophile. Can. J. of Chem., *48*, 1351-1357 (1970).

28. Davis, G. T., Demek, M. M., Sowa, J. R., and Epstein, J. Solvent Effects on Displacement of Fluoride Ion from Isopropyl Methylphosphonofluoridate. J. Am. Chem. Soc., *93*, 4093-4103 (1971).

29. Wagner, P. T., and Lew, M. Carbon Dioxide Content of Ethanolamine Solutions. Anal. Chem., *26*, 575-576 (1954).

30. Layan, F., and Felong, B. Apparatus and Method for Determining Alkanolamine-Continued Hydrogen Sulfide or Carbon Dioxide. C.A., *79*, 38335g (1973).

DISTRIBUTION LIST 4

Names	Copies
EDGEWOOD ARSENAL	
FOREIGN INTELLIGENCE OFFICER	1
CHIEF, LEGAL OFFICE	1
CHIEF, SAFETY OFFICE	1
CHIEF, PLANS OFFICE	
Attn: DRDAR-CLR-L	1
CDR, US ARMY TECHNICAL ESCORT CENTER	1
AUTHOR'S COPY, Chemical Laboratory	4
BIOMEDICAL LABORATORY	
Attn: SAREA-BL-M	1
Attn: SAREA-BL-O	1
Attn: SAREA-BL-Q	1
Attn: SAREA-BL-R	1
Attn: SAREA-BL-RC	1
Attn: SAREA-BL-RE	1
Attn: SAREA-BL-RI	1
Attn: SAREA-BL-V	1
CHEMICAL LABORATORY	
Attn: SAREA-CL	1
Attn: SAREA-CL-B	1
Attn: SAREA-CL-BS	1
Attn: SAREA-CL-C	1
Attn: SAREA-CL-D	1
Attn: SAREA-CL-P	1
Attn: SAREA-CL-TE	1
DEVELOPMENT AND ENGINEERING DIRECTORATE	
Attn: SAREA-DE-D	1
Attn: SAREA-DE-EP	1
Attn: SAREA-DE-ET	1
Attn: SAREA-DE-M	1
Attn: SAREA-DE-N	1
MANUFACTURING TECHNOLOGY DIRECTORATE	
Attn: SAREA-MT-D	1
Attn: SAREA-MT-E	1
Attn: SAREA-MT-P	1
DIRECTOR OF PRODUCT ASSURANCE	
Attn: SAREA-PA-A	1
Attn: SAREA-PA-P	1
Attn: SAREA-PA-Q	1
DIRECTOR OF TECHNICAL SUPPORT	
Attn: SAREA-TS-R	2
Attn: SAREA-TS-L	3
Attn: SAREA-TS-E	1

Names	Copies
DEPARTMENT OF DEFENSE	
Administrator	
Defense Documentation Center	
Attn: Accessions Division	2
Cameron Station	
Alexandria, VA 22314	
Director	
Defense Intelligence Agency	
Attn: DB-4G1	1
Washington, DC 20301	
DEPARTMENT OF THE ARMY	
HQDA (DAMO-SSC)	1
WASH DC 20310	
Director	
Defense Civil Preparedness Agency	
Attn: RE	1
Attn: PO(DC)	1
Washington, DC 20301	
CINCUSAREUR	
Attn: AEAGC-DS	1
APO New York 09403	
Chief, Office of Research, Development & Acquisition	
Attn: DAMA-CSM-CM	1
Attn: DAMA-ARZ-D	1
Washington, DC 20310	
Headquarters, Sixth US Army	
NBC Office	
Attn: AFKC-OP-PN	1
Presidio of San Francisco, CA 94129	
HQDA (DAMI-FIT)	1
WASH, DC 20310	
US ARMY HEALTH SERVICE COMMAND	
Commander	
US Army Environmental Hygiene Agency	
Attn: HSE-AA-L, Librarian, Bldg 2100	1
APG-Edgewood Area	
Superintendent	
Academy of Health Sciences	
US Army	
Attn: HSA-CDC	1
Attn: HSA-IHE	1
Fort Sam Houston, TX 78234	

DISTRIBUTION LIST 4 (Contd)

Names	Copies
US ARMY MATERIEL DEVELOPMENT AND READINESS COMMAND	
Commander US Army Materiel Development and Readiness Command Attn: DRCDE-DM Attn: DRCLDC Attn: DRCMT Attn: DRCSF-S 5001 Eisenhower Ave Alexandria, VA 22333	1 1 1 1
Commander US Army Foreign Science & Technology Center Attn: DRXST-IS1 220 Seventh St., NE Charlottesville, VA 22901	2
Project Manager for Chemical Demilitarization and Installation Restoration Attn: DRCPM-DR, Bldg E4585 APG-Edgewood Area	1
Redstone Scientific Information Center Attn: Chief, Documents US Army Missile Command Redstone Arsenal, AL 35809	1
Director DARCOM Field Safety Activity Attn: DRXOS-C Charlestown, IN 47111	1
US ARMY ARMAMENT COMMAND	
Commander US Army Armament Command Attn: DRSAR-ASN Attn: DRSAR-IMB-C Rock Island, IL 61201	1 1
Commander US Army Dugway Proving Ground Attn: Technical Library, Docu Sect Dugway, UT 84022	1
Commander Rocky Mountain Arsenal Attn: SARRM-EA Attn: SARRM-MD Denver, CO 80240	1 1
Commander Pine Bluff Arsenal Attn: SARPB-ETA Pine Bluff, AR 71611	1

Names	Copies
US ARMY TRAINING & DOCTRINE COMMAND	
Commandant US Army Infantry School Combat Support & Maintenance Dept. Attn: NBC Division Fort Benning, GA 31905	1
Commandant US Army Missile & Munitions Center & School Attn: ATSK-CD-MD Attn: ATSK-DT-MU-EOD Redstone Arsenal, AL 35809	1 1
Commandant US Army Military Police School Attn: ATZN-CD Fort McClellan, AL 36205	1
Chief, Training Literature Division Attn: ATZN-TDP Fort McClellan, AL 36205	1
Headquarters US Army Military Police School/Training Center Attn: ATSJ-TD-CR Fort McClellan, AL 36205	1
Commander US Army Infantry Center Attn: ATZB-CD-MS-C Fort Benning, GA 31905	1
Commandant US Army Ordnance Center & School Attn: ATSL-CD-MS Attn: ATSL-DTG APG-Aberdeen Area	1 1
US ARMY TEST & EVALUATION COMMAND	
Record Copy CDR, APG Attn: STEAP-AD-R/RHA APG-Edgewood Area, Bldg E5179	1

DISTRIBUTION LIST 4 (Contd)

Names	Copies
CDR, APG Attn: STEAP-TL APG-Aberdeen Area	1
Commander US Army Test & Evaluation Command Attn: DRSTE-FA APG-Aberdeen Area	1
Commander US Army Cold Regions Test Center Attn: STECR-TD APO Seattle 98733	1
Commander US Army Tropic Test Center Attn: STETC-MO-A (Tech Library) APO New York 09827	1
Commander Dugway Proving Ground Attn: STEDP-PO Dugway, UT 84022	1
DEPARTMENT OF THE NAVY	
Chief of Naval Research Attn: Code 443 800 N. Quincy Street Arlington, VA 22217	1
Commander Naval Facilities Engineering Command Attn: Code 03 200 Stovall Street Alexandria, VA 22332	1
Commander Naval Explosive Ordnance Disposal Facility Attn: Army Chemical Office Indian Head, MD 20640	1
Commander Naval Surface Weapons Center Attn: Tech Lib & Info Svcs Br White Oak Laboratory Silver Spring, MD 20910	1
Commander Naval Surface Weapons Center Dahlgren Laboratory Attn: DX-21 Dahlgren, VA 22448	1
Commander Nuclear Weapons Training Group, Atlantic Naval Air Station Attn: Code 21 Norfolk, VA 23511	1
Chief, Bureau of Medicine & Surgery Department of the Navy Attn: CODE 5 Washington, DC 20372	1
Commander Naval Weapons Center Attn: A. B. Galloway/Code 3171 Attn: Technical Library/Code 233 China Lake, CA 93555	1 1
DEPARTMENT OF THE AIR FORCE	
Air University Library Attn: AUL/LSE-8879 Maxwell AFB, AL 36112	1
HQ Foreign Technology Division (AFSC) Attn: PDRR Wright-Patterson AFB, OH 45433	1
Commander Aeronautical Systems Division Attn: ASD/AELD Wright-Patterson AFB, OH 45433	1
HQ, USAF/SGPR Forrestal Bldg WASH DC 20314	1
HQ, USAF/RDPN WASH DC 20330	1
HQ, Ogden ALC/MMWRA Hill AFB, UT 84406	1
Director Air Force Inspection and Safety Center *Attn: IGD(AFISC/SEV)* Norton AFB, CA 92409	1
Commander Armament Development & Test Center Attn: DLOSL (Technical Library) Eglin AFB, FL 32542	1
NORAD Combat Operations Center/DBN Cheyenne Mtn Complex, CO 80914	1
OUTSIDE AGENCIES	
Battelle, Columbus Laboratories Attn: TACTEC 505 King Avenue Columbus, OH 43201	1
Director of Toxicology National Research Council 2101 Constitution Ave, NW Washington, DC 20418	1

REVIEW OF INFORMATION/INFORMATION MATERIALS PAO-99-362

1. AUTHOR/COTR Extension Office Symbol
Paul M. Davis
Richard L. Kipp
Marguerite E. Brooks

2. MATERIAL CLASSIFICATION
(Circle one): (UNCL) CONF SECRET
Distribution Limited

3. TYPE OF MATERIAL.
X Technical Report
__ Technical Note
__ Oral Presentation
__ Poster Session
__ Contractor Report
__ Special Publication
__ Abstract
__ Other

4. FUNDING CATEGORY (Circle one)
6.1 6.2 6.3. 6.4
6.5 Customer Other
(if customer, please identify)

5. TITLE. Technical Report ARCSL-TR-79004
Decontaminating Solution for the disposal of Identification and Training Sets

6. TYPE OF RELEASE.
X UNLIMITED DISTRIBUTION. Statement A (Public Release)
__ LIMITED DISTRIBUTION. Select statement below (check one only) and give applicable reason (see chart on page 4 of this form)
__ B - U.S. Government agencies only
__ C - U.S. Government agencies and their contractors only
__ D - DoD and U.S. DoD contractors only
__ E - DoD Components only
__ F - Further dissemination only as directed by Cdr, Chemical and Biological Defense Command (CBDCOM) or his designee.
__ X - U.S. Government agencies and private individuals or enterprises eligible to obtain export-controlled technical data
REASON: Utah Chemical Agent Rule Repository

__ Classified Material

Security Classification Authority, CLASSIFIED BY: _____

Declassification or Downgrading Instructions, DECLASSIFY ON: _____
DOWNGRADE ON: _____

7. Attached will____will not____be presented to foreign nationals or presented at a symposium where foreign nationals or foreign representatives will be present. (If answer is "will" or "unknown", contact the Counterintelligence Office (Foreign Disclosure) for assistance.) (For Limited Distribution Only)

8. Name and address of periodical (if for journal publication):
_____
_____
_____Refereed _____Non refereed

9. Forum: _____
Title: _____
Location _____
Date. _____
DoD sponsored: __Yes __ No

10. Attached has____has not____been coordinated with contractor. Name and address of contractor:
_____
_____
_____

11. Invention/work described herein has___ has not____been forwarded to Office of the Chief Counsel CBDCOM
Name of inventor _____
Organization _____
File Number of Invention _____

12. Portion of attached was __ was not__ extracted from copyrighted source.
Source Documentation: _____
Permission granted by _____
(Correspondence Attached)

13. APPROVAL RECOMMENDED:

a. Technical Merit

b. Security Classification and Markings Included

c. Data Exchange Agreements/ Memo of Understanding

d. Proper Distribution Markings

e. Patentability /Inventions

f. Contractor Imposed Limited Rights (Proprietary)

g. Confidentiality of Any Contractor or Customer Data

h. News Media/Public Release

i. Required Caveats for Open Literature Publication

j. Operations Security

In reviewing the attached information material, I have considered the above areas and recommend approval:

Team Leader/Division/Office Chief — 26 Jan 99 (Date) — 5-1895 (Extension)

14. SECURITY REVIEW:

✓ Approved ___Disapproved ___See Comments

Counterintelligence Office Reviewer — 4 May 99 (Date) — 3549 (Extension)

15. MILITARILY CRITICAL TECHNOLOGY LIST (MCTL):

___Approved ___Disapproved ___See Comments

MCTL Reviewer — Date — Extension

16. FOREIGN INTELLIGENCE (FI) REVIEW:

✓ Approved ___Disapproved ___See Comments

FI Office Reviewer — 6 May 99 (Date) — 3273 (Extension)

17. INTERNATIONAL PROGRAMS (IP) REVIEW:
(Required for Technical & Special Reports)

TTCP-E - Yes No ... MOU - Yes No Other

IP Office Reviewer — Date — Extension

18. I, the undersigned, am aware of the foreign intelligence interest in open source publications and in the subject matter of the information I have reviewed for OPSEC purposes. I certify that I have sufficient technical expertise in the subject matter of this report/paper and that, to the best of my knowledge, the net benefit of this public release outweighs the potential damage to the essential secrecy of all related CBDCOM, Army, or other government programs of which I am aware.

Recommend release as ___UNCLASSIFIED UNLIMITED.

Director/PM/PD/Office Chief — Date — Extension

Approve release as ___UNCLASSIFIED LIMITED, or ___CLASSIFIED.

19. PUBLIC RELEASE.

X APPROVED FOR PUBLIC RELEASE ___FORWARDED FOR HIGHER HEADQUARTERS REVIEW

Chief, Public Affairs Office — 6/21/99 (Date) — X5-5394 (Extension)

20. COMMENTS.

AD

TECHNICAL REPORT ARCSL-TR-79004

DECONTAMINATING SOLUTION FOR THE DISPOSAL OF IDENTIFICATION AND TRAINING SETS

by

Paul M. Davis
Richard L. Kipp
Marguerite E. Brooks

Research Division

and

Michael L. Duggan

Munitions Division

April 1979

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-79004	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DECONTAMINATING SOLUTION FOR THE DISPOSAL OF IDENTIFICATION AND TRAINING SETS		5. TYPE OF REPORT & PERIOD COVERED Technical Report July 1977–August 1978 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Paul M. Davis, Marguerite E. Brooks Richard L. Kipp, Michael L. Duggan		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander/Director, Chemical Systems Laboratory Attn: DRDAR-CLB-R Aberdeen Proving Ground, Maryland 21010		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Demil Tech 728012.21 Work Order No. 31V4-01
11. CONTROLLING OFFICE NAME AND ADDRESS Commander US Army Toxic and Hazardous Materials Agency Attn: DRXTH-TS Aberdeen Proving Ground, Maryland 21010		12. REPORT DATE April 1979 13. NUMBER OF PAGES 38
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to US Government agencies only because of test and evaluation; April 1979. Other requests for this document must be referred to Commander, US Army Toxic and Hazardous Materials Agency, Attn: DRXTH-TS, Aberdeen Proving Ground, Maryland 21010.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Chemistry of agents
Demilitarization of agents
Disposal of chemical agent identification and training sets

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

(U) Chemical agent identification and training sets (CAITS)
Demilitarization
Flash point
Reaction time
Chloropicrin (PS)
Decontamination
Ethylene glycol monomethyl ether
M-8 detector paper
Commercial bleach
Methyl cellosolve
Lewisite (L, M-1)

(Continued on reverse side)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(U) Demilitarization and disposal of obsolete war gas identification and training sets will use an incineration process. The sets contain mustard (HD), lewisite (L), cyanogen chloride (CK), phosgene (CG), chloropicrin (PS), and nerve agent (GB), as well as chloroform, chloroacetophenone (CN), diphenylamine chloroarsine (DM), and some agent simulants. The sets will be disassembled to remove the cans containing the agent. The cans will then be fed directly into a furnace. The disassembly operation will probably result in some agent contamination inside the glove box from leaking cans. Contamination outside the glove box was also a consideration.

(Continued on reverse side)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19. KEYWORDS (Contd)

Mustard (HD)
Solubility
Sodium hypochlorite
Material compatibility
Polyurethane

20. ABSTRACT (Contd)

Two decontaminating solutions were tested for effectiveness in removing agent from the surfaces of materials where possible contamination would occur. These materials include: stainless steel (glove box), carbon steel – painted and unpainted (shipping containers), lead (gaskets), and coated concrete (floor in glove box area). These solutions were 30 volume parts of 50% (w/w) aqueous sodium hydroxide to 70 volume parts of methyl cellosolve and 5% (w/w) aqueous sodium hypochlorite (commercial bleach).

The decontamination studies demonstrated that:

1. The decontaminating solutions meet the criteria established for use in the disposal operation of identification and training sets.

2. The most effective decontaminating procedure for using the sodium hydroxide/methyl cellosolve solution is to wipe the agent from the surface with paper towels, swab the contaminated surface with decontaminant, wait 5 minutes, wipe off the decontaminant with paper towels, and swab and wipe the surface two more times with no waiting period between them.

This report gives a description of the development and testing of the decontaminating solutions. Included are the determination of flash points, relative solubilities, and reaction rates. Also presented are the results demonstrating the effectiveness of the decontaminating solutions. Finally, information concerning how to mix the decontaminating solutions, when and how to use the solutions, how to check the activities of the solutions, and how to handle the solutions safely is compiled in appendix B.

PREFACE

The work described in this report was authorized by the Project Manager for Chemical Demilitarization and Installation Restoration under Work Order No. 31V4-01, Decontamination Studies. This work was started in July 1977 and completed August 1978.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Acknowledgments

The authors acknowledge the contributions of Mr. James W. Goheen and Mr. Nicholas J. Rescigno for planning and technical guidance of the studies, Mr. Rinaldo J. Bucci and Mr. John Scott for program management, Mrs. Rovena C. Holmes for editing the report, and Mrs. Opal S. Ragno for typing assistance.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

DECONTAMINATING SOLUTION FOR DISPOSAL OF IDENTIFICATION AND TRAINING SETS

I. INTRODUCTION.

Disposal of the war gas identification and training sets at Rocky Mountain Arsenal (Denver, Colorado) will be performed at the Honest John Facility (bldg 1611). Partial disassembly of the steel shipping cylinders (pigs) will be necessary to remove the cans of agent which are fed directly into the deactivation furnace.

The procedure for disassembly of the pigs and disposal of the agents and contaminated parts is illustrated in the flow chart (figure 1). The sets are shipped from the storage area and transferred through the holding area into the glove box area. The disassembly procedure begins by installing the pig with the flanged portion sealed inside the disassembly section. After the flange cover plate and the lead gasket are removed, the cans are transferred from the pig to the inside of the disassembly module. The cans proceed to the storage module on a screw conveyor where they are fed into the deactivation furnace. The lead gasket and five bolts and nuts are placed back into the pig which is then resealed with the three remaining bolts and nuts. Pigs which contain leaking cans of agent will be immediately decontaminated before being sent to the decontaminating furnace to prevent the spreading of gross contamination of agent.

A liquid agent leak from a pig outside the glove box would also require immediate decontamination to minimize any resulting interruption of the disposal operation. But this type of contamination also surfaces the problem of possible seepage of agent into the concrete floor in the glove box area. If contamination did occur, the only means of assuring complete decontamination of the floor would be to physically remove the section of the floor involved. To avoid this drastic measure, the floor of the glove box area will be coated with a substance which is determined to be the most compatible with the agents and the decontaminant solution. Liquid agent which leaks from a pig inside the glove box will collect on the glove box floor. Since the agent is contained in a well-ventilated enclosure (600 acfm at 24.4-inch Hg and 70°F), immediate decontamination will not be required.

The selection of a decontaminant was not only complicated by the various applications for which it was required but also by the number of agents with which it must react without interfering with the detection methods. Other criteria which were considered in the selection of a decontaminant were as follows:

1. The decontaminant solution would be soluble in water.

2. The decontaminant solution would be miscible with the agent and chloroform.

3. The decontaminant solution would have a relatively large capacity to neutralize the agents and chloroform.

4. The decontaminant solution would be noncorrosive with the metals in the glove boxes and the floor coating.

5. The decontaminant solution would not be hazardous to personnel (high flash point, minimal toxicity).

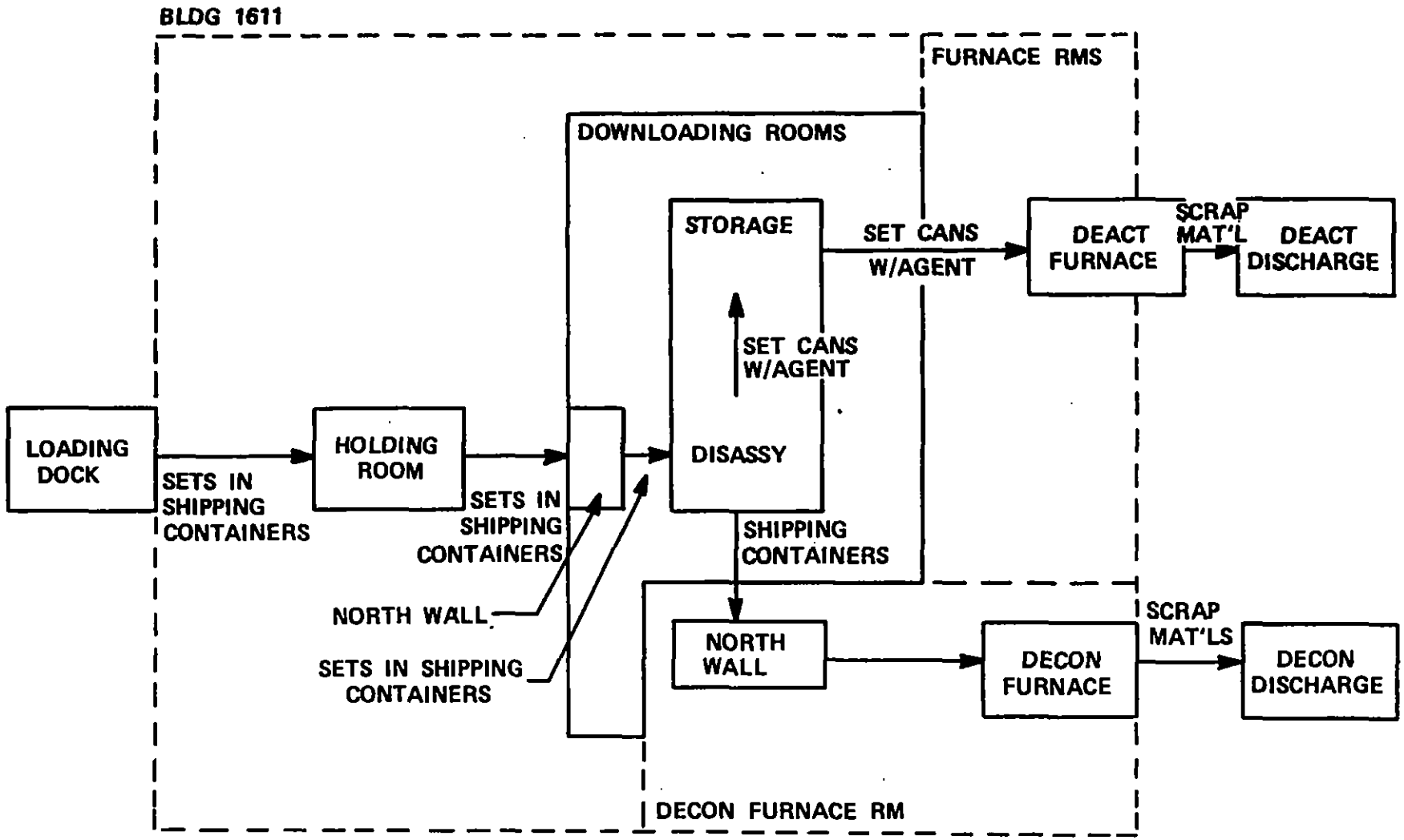


Figure 1. K941/942, K951/952, K953/954 Identification Set Process Flow Diagram

Several standard decontaminants now being used by the US Army (STB, HTH, DS-2, DANC), in addition to other decontaminants (aqueous sodium hydroxide, alcoholic sodium hydroxide, monoethanolamine), were considered. Unacceptable chemical or physical characteristics of the individual decontaminants eliminated each one for application in the disassembly module. Aqueous solutions of sodium hydroxide, STB, and HTH are not miscible with all the agents which results in a very slow reaction. The use of either DS-2, which contains an amine, or monoethanolamine would require additional detection procedures to monitor for the low threshold limit values (TLV) of the amines (4 to 6 mg/m^3). Detection and monitoring of one more material would only complicate the requirements already existing for seven other compounds. DANC solution consists primarily of acetylene tetrachloride (1,1,2,2-tetrachloroethane) which is highly toxic (TLV = 35 mg/m^3) and would also require monitoring. STB and HTH solutions are highly corrosive and liberate chlorine gas which would interfere with some of the detection methods (chloroform, phosgene) (appendix A).

To meet the requirements for the decontamination of an agent release within the glove box and an agent spill on the work-area floor surrounding the glove box, it was judged that possibly two decontamination solutions and procedures would be necessary. The primary purpose of the decontaminating solution used inside the glove box was to solvate the agent, after which the major part of it could be removed with absorbent paper towels. The towels would be inserted into a fiber overpack for incineration. Excess decontaminant solution would be flushed from the area with water and stored in a holding tank to allow for the reaction of residual agent.

Another important characteristic was that it would not interfere with the agent detection procedures. The solution used outside the glove box would have to react with the agent within 5 to 10 minutes. It would also have to be compatible with the floor coating. Interference with the detection methods was not as critical in this situation because the personnel performing the decontamination would be dressed in adequate protective clothing. Any residual decontaminant would be completely wiped away and the vapors carried away with the ventilation air before detection procedures were restarted to verify a clean area.

Several decontaminants were considered for use inside the glove box. All of these consisted of a combination of a solvent and aqueous sodium hydroxide. To meet the proposed requirements, the solvent used in the decontaminating solution would have to be nonreactive with sodium hydroxide, soluble in water, and essentially nonflammable (high flash point) and nontoxic (high TLV). To be effective, the solvent would have to be miscible with water, sodium hydroxide, and mustard. The solvents considered were basically glycols, cellosolves, and carbitols.

Only two types of solutions were considered for agent spills outside the glove box. These were aqueous sodium hypochlorite (commercial bleach) and the decontaminant selected for the inside of the glove box. Once the decontaminant solutions were selected, tests were performed to determine the effectiveness of each in decontaminating samples of materials from the glove box, pigs, and floor coating.

This report presents the experimental work performed in the development and testing of the decontaminant solutions. The preliminary work involved the selection of an adequate solvent which included the determination of flash points, solubilities, and reaction rates. This was followed by studies to determine the effectiveness of the decontaminant solutions. Appendix B of this report resents information required in the actual use of the decontaminant. This information includes recommendations on how to mix the solution, when and how to use the solution, how to check the activity of the solution, and how to safely handle the solution.

II. EXPERIMENTATION.

A. Solvent Selection.

1. Solubility Tests.

These tests consisted of mixing a neat solvent and 50% (w/w) sodium hydroxide and allowing the solution to sit for 24 hours. The solution was then visually checked to determine homogeneity. The solutions tested were 70 to 30 volume parts and 80 to 20 volume parts of solvent to aqueous sodium hydroxide, respectively. Those solvents which passed this portion of the test were checked for solubility with neat mustard and then with chloroform. A discussion of the results of these tests is presented in section III.A.1.

2. Flammability Tests.

After the solubility tests were completed, the solvent/caustic solution had to be tested for its flash point. This was to insure that the solution was not hazardous for use within the glove box. These tests were conducted by ASTM Procedure Nos. D56 for closed-cup flash point and D1310 for the open-cup flash point. These results are presented in section III.A.2.

3. Reaction Rate Tests.

The solvent/caustic solution selected was then tested for its effectiveness in destroying agent. Since mustard presented the major problem of miscibility in aqueous solutions, it was chosen for use in these tests. The proportions of solvent to caustic were varied to determine an optimum solution. These results are discussed in section III.A.3.

4. Detector Paper Tests.

Once the solution was applied, a detection method was required to determine that complete decontamination was achieved. The M-8 liquid agent detector paper was suggested, and a simple test was devised to check for interferences from other chemicals which may be present during the disposal operation. The results of these tests are discussed in section III.A.4.

B. Decontamination Tests.

These tests were performed using samples of materials representative of both the painted and unpainted mild steel surfaces of the pigs, the lead gaskets used to seal them, the stainless steel of the glove box, and coated concrete for the floor. The chemical agents tested consisted of neat mustard (HD), neat lewisite (L), and neat chloropicrin (PS). Four or five tests were performed with both neat mustard and mustard in chloroform with no discernible differences. Therefore, all the agents were tested in the neat form.

1. Materials.

a. 316 Stainless steel: 3- by 3-inch samples

b. Low carbon steel: 3- by 3-inch samples

c. Lead: 3- by 1-inch samples

d. Coated concrete: 3- by 3- by 1-inch concrete samples coated (approximately 0.015 inch thick) with white Chemglaze II Polyurethane (No. A276) over Wash Primer (No. 9924) manufactured by Hughson Chemicals, Lord Corporation, Erie, Pennsylvania 16512.

2. Equipment.

A Hewlett-Packard Model No. 5830A gas-liquid chromatograph with flame ionization detector was used for agent analysis. A 6-foot column consisting of 10% UCW982 on 80-100 mesh high-performance Chromasorb W was chosen for all analyses. Instrument temperatures and flow rates are shown in table 1. These data were selected to give minimum run times while maintaining the detectable peak resolution (table 2).

3. Standard Solutions.

The standards for mustard and chloropicrin were prepared by weighing several drops of the agent in 10 ml of hexane and making the appropriate dilutions. The lewisite standard was prepared by pipetting 0.1 ml of the agent into 100 ml of hexane and making dilutions. A liquid density for lewisite of 1.89 gm/cc at 20°C was used to determine the milliliters of agent required. The solvent was Fisher Spectranalyzed Hexane containing methylcyclopentane isomer (certified ACS quality) and gave a minimum number of solvent peaks on the gas-liquid chromatograph. Table 2 shows the concentrations used for each agent and the retention times experienced at various temperatures.

4. Procedure.

Representative samples were contaminated with 1 to 5 μl of agent. The agent was wiped from the surface with absorbent paper towels. The surface was then swabbed with the decontaminant solution. After 5 minutes, the decontaminant was wiped off with paper towels, and the surface was swabbed and wiped two more times with no waiting period between them. The surface was rinsed with 10 ml of hexane of which a 10-μl aliquot was analyzed in the gas-liquid chromatograph. A control sample was run with each test. With one exception, this sample was subjected to the same conditions as those of the test samples mentioned above. The sample was not decontaminated before being rinsed with the hexane. A discussion of the results of these tests are presented in section III.B.

Some effort was made to optimize on the procedure. Variations in the number of applications required and the amount of time which the decontaminant remained on the surface were examined. Neat mustard (HD) was selected for these tests because it was the most persistent. The results of the effort are discussed in section III.B.

Table 1. Chromatograph Operating Parameters

Agent	Column temperature	Injection port temperature	Flame ionization detector temperature	Flow rate	Carrier gas
	°C	°C	°C	ml/min	
Mustard (HD)	150	225	300	30	Helium
Lewisite (L)	135	185	300	45	Helium
Chloropicrin (PS)	90	200	300	45	Helium

Table 2. Chromatograph Response to Standard Solutions

Agent	Solvent	Concentration	Column temperature	Retention time	Peak area
		ppm	°C	min	
HD	Hexane	150	150	2.19	40520
				2.31	38490
				2.32	41060
				2.33	44340
		75	150	2.24	16620
		15	150	2.16	2190
				2.16	2306
		7.5	150	2.16	1097
				2.16	1147
				2.13	1076
		1.5	150	2.16	180
				2.16	193
				2.16	232
				2.16	201
				2.16	216
Lewisite (L)	Hexane	1890	135	2.17	220400
		189	135	2.07	9336
			135	2.18	8774
		38	125	2.83	457
				2.87	405
				2.84	430
		19	135	2.13	76
				2.13	70
Chloropicrin (PS)	Hexane	440	85	2.13	13400
			85	2.17	13500
			85	2.13	12720
			90	1.67	13470
				1.65	13700
				1.67	14110
		88	90	1.65	217
				1.65	206
				1.65	230

II. RESULTS AND DISCUSSION.

A. Solvent Selection.

1. Solubility Tests.

Several solvents were selected as the most likely to meet the established criteria. Ethyl and methyl carbitol were the first solvents eliminated because they were not miscible with 50% (w/w) sodium hydroxide. The other solvent/sodium hydroxide mixtures were then tested for solubility with neat mustard (HD) (table 3). The only two mixtures which were soluble with neat mustard were ethyl cellosolve/sodium hydroxide and methyl cellosolve/sodium hydroxide. Of the two remaining mixtures, only methyl cellosolve/aqueous sodium hydroxide formed a homogeneous solution with 25 vol % chloroform in both an 80/20 ratio and a 70/30 ratio of solvent to sodium hydroxide, respectively.

Table 3. Solubility Tests

Solvent	Solubility		
	50% NaOH[a]	HD[b]	$CHCl_3$[c]
Ethylene glycol	Yes	No	–
Diethylene glycol	Yes	No	–
Methyl cellosolve	Yes	Yes	Yes
Ethyl cellosolve	Yes	Yes	Yes
Methyl carbitol	No	–	–
Ethyl carbitol	No	–	–
Propylene glycol	Yes	No	–

[a] To form a homogeneous solution with 20 to 30 parts 50% NaOH.

[b] 100 ml of 20 parts 50% NaOH and 80 parts solvent would dissolve 0.25 ml HD within 3 minutes with stirring.

[c] 20 Parts of 50% NaOH and 80 parts of solvent also formed a homogeneous solution with chloroform in the ratio of 25 volume parts of chloroform to 75 volume parts of decontaminating solution.

The 80% ethyl cellosolve/20% aqueous sodium hydroxide also formed a solution with chloroform in the ratio of 25 volume parts of chloroform to 75 volume parts of decontaminating solution. The 70% ethyl cellosolve/30% aqueous sodium hydroxide became cloudy when 24 volume parts of chloroform was added to 76 volume parts of decontaminating solution. Two layers were observed when 27 volume parts of chloroform was added. The second layer increased to 10 vol % in 1.5 hours and to 20 vol % in 20 hours. Nevertheless, it was judged that the ethyl cellosolve has adequate solubility for the proposed applications and could be used if methyl cellosolve is not available.

The decontaminant/chloroform solutions showed some signs of a reaction occurring over a 24-hour period. A slow release of bubbles was observed with no change in the temperature of 100 ml of solution. Previous studies have shown that chloroform and sodium hydroxide react to produce carbon monoxide as one of its products.[1] It was judged that the bubbling action during this phase of the tests was a result of carbon monoxide being formed. As a result, this mixture cannot be stored in a sealed container without risking a rupture of the container from an internal pressure build-up.

2. Flammability Tests.

The open-cup and closed-cup flash points were determined for neat methyl cellosolve and two formulations of methyl cellosolve and 50% (w/w) aqueous sodium hydroxide. These data are presented in table 4 in addition to values reported in literature for neat methyl cellosolve. For comparison purposes, the flash points for other familiar materials are also listed.

Table 4. Flash Point

Solvent	Open cup	Closed cup
	°F	°F
Methyl cellosolve	115*	107*
80% Methyl cellosolve/20% aqueous sodium hydroxide	120	108
70% Methyl cellosolve/30% aqueous sodium hydroxide	155	120
DS-2 solution	148	168**
Ethyl cellosolve	120*	106*
No. 2 fuel oil	–	110-190*
Kerosene (No. 1 fuel oil)	–	100-165*
Gasoline	–	-50*

*Literature value.

**Specification Mil-D-50030D(MU).

The analytical personnel were unable to explain the apparent discrepancy between the flash points associated with the DS-2 solution, i.e., a higher value for the closed-cup flash point relative to the open-cup value. Nevertheless, comparing the open-cup flash points of the DS-2 solution and the recommended cellosolve/caustic solution shows only a 7°F difference. As compared with the other materials listed, the closed-cup flash point of cellosolve/caustic solution (70/30 parts by volume) is in the lower range of the values reported for No. 2 fuel oil and kerosene.

[1] Roberts, John D., and Caserio, Marjorie C. Basic Principles of Organic Chemistry. W. A. Benjamin, Inc., New York, New York. 1964.

A small laboratory experiment was performed to determine the potential hazard of a flash fire in using the cellosolve/caustic solution (70/30 parts by volume). The primary hazard was thought to exist whenever pigs were stored in the decontaminant conveyor shroud while other pigs were being fed into the decontaminant furnace through an open door.

One edge of a paint can lid was dipped into the proposed decontaminating solution and gradually brought to a Bunsen burner flame in a darkened room. No flash was observed from the decontamination solution until it was immersed in the flame. The decontaminating solution did not burn until the flame had warmed the metal and the solution. Therefore, no flash hazard is expected when using the decontaminating solution in any area where there is a minimal airflow to prevent an accumulation of vapors and no source of ignition.

3. Reaction Rate Tests.

In order to optimize the quantities of caustic solution and methyl cellosolve required for decontamination, the reaction rates were determined for mustard in methyl cellosolve and various concentrations of caustic solution in methyl cellosolve. The decontaminating solutions consisted of different concentrations of 50% (w/w) aqueous sodium hydroxide, water, and methyl cellosolve. Table 5 shows the quantity of each material used to prepare each of the four solutions tested. Solutions containing more than 13% to 14% sodium hydroxide were not used in the rate studies because solution E gelled during mixing. Also, the reaction rate of mustard in a chloroform solution could not be studied because the reaction of caustic and chloroform would obscure the mustard reaction. Therefore, a solution of neat mustard (HD) in methyl cellosolve was prepared containing 50 mg HD/ml.

Table 5. Decontaminating Solutions

Solution	50% NaOH	Water	Methyl cellosolve	NaOH	Water	Methyl cellosolve
	ml	ml	ml	wt %	wt %	wt %
A	10	10	80	7.5	17.2	75.3
B	20	20	60	14.1	32.6	53.3
C	30	30	40	20.1	46.3	33.6
D	30	–	70	20.3	20.3	59.4
E	40	–	60	25.7	25.7	48.6

For each of the rates studied, a 2-ml aliquot of the mustard solution was added to 10 ml of the decontaminating solution. At designated times, 50 ml of 3N nitric acid was added to the mixture to stop the reaction. The chloride ion liberated during the reaction was determined by the standard Volhard titration procedure. To determine the percent mustard destroyed, it was assumed that both chlorine atoms were being removed simultaneously from the mustard molecule during the reaction. The percent of the mustard destroyed was then plotted versus reaction time (figure 2).

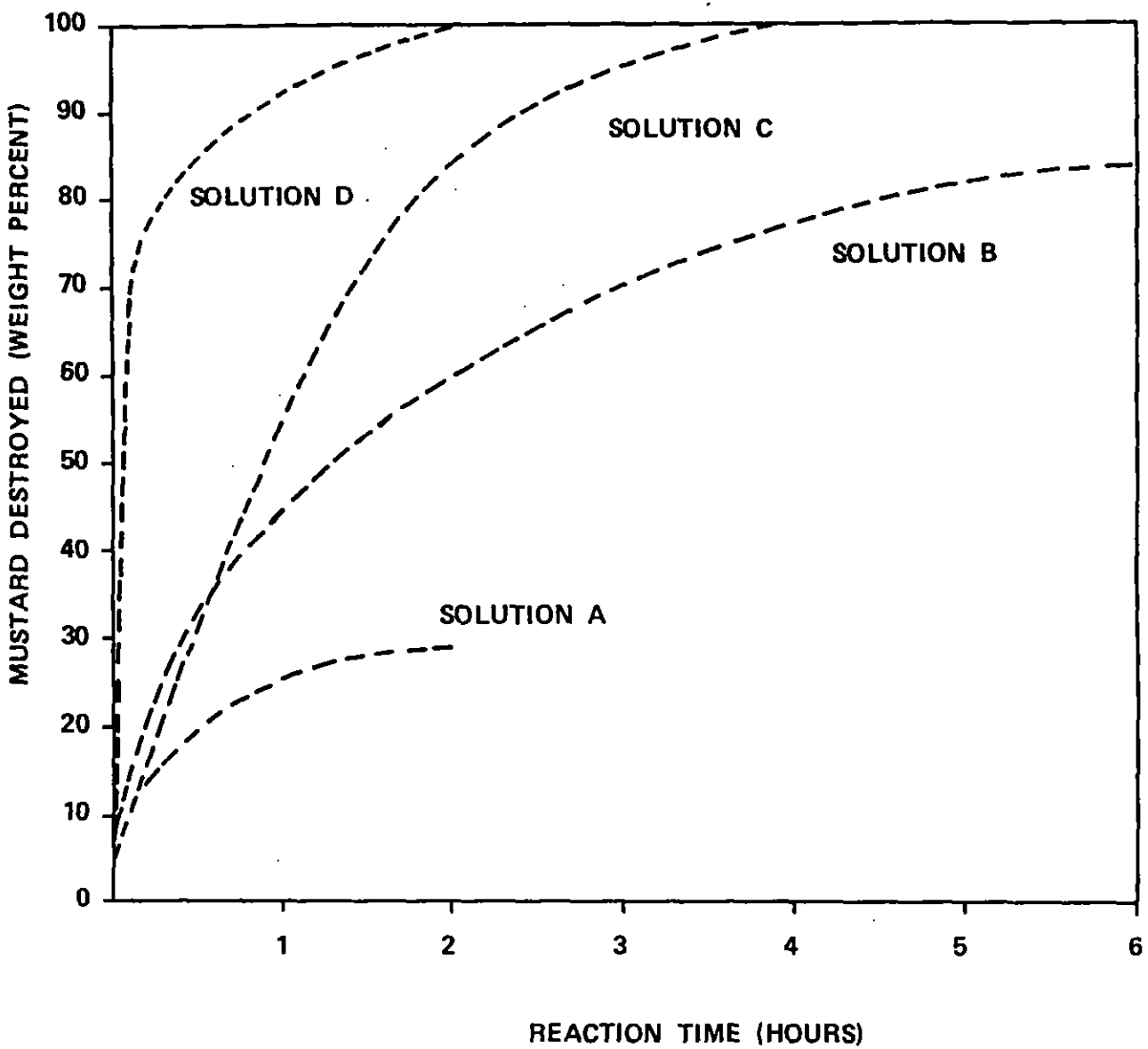


Figure 2. Reaction of Neat Mustard with Sodium Hydroxide in Methyl Cellosolve

The reaction of mustard with solution A was very slow with only 29 wt % of the agents being destroyed after 2 hours. The reaction mechanism being followed by solution B is thought to be the removal of the first chlorine at a fast rate followed by a slower rate for the second chlorine. Only 84 wt % of the mustard was destroyed after 6 hours. Theoretically, complete destruction of the mustard would require 12 hours with solution B. Samples allowed to stand overnight (18 hours) showed complete destruction of the agent. Solution C has the same initial reaction rate as solution B and apparently continues at the same reaction rate up to approximately 80 wt % destruction. Then the slower secondary reaction rate is observed until the agent is completely destroyed at 4 hours. This could simulate the reaction time which would be expected whenever large amounts of water are used to wash down the decontaminant from the pigs or from the walls of the glove boxes. Complete destruction of mustard in solution D was obtained in 2 hours at approximately 70° to 80°F. Stoichiometrically, the sodium hydroxide in 100 ml of solution D will neutralize 29.8 grams of mustard as follows:

$$(ClCH_2CH_2)_2S + 2\ NaOH \rightarrow 2\ NaCl + (HOCH_2CH_2)_2S$$

4. Detector Paper Tests.

The M-8 detector paper was tested by simply applying a few drops of various chemicals to the paper and observing the resulting color change. Methyl cellosolve gave a yellow indication which could be misinterpreted by untrained personnel as showing the presence of the nerve agent GB.

The methyl cellosolve/sodium hydroxide solution turns the M-8 paper very dark green or black. Minute yellow specks were observed in the dark green spot in one test and a yellow fringe was observed around the spot in another test. It is thought that this color change could be misinterpreted as an indication of the nerve agent VX, and where traces of yellow were observed both VX and GB could be falsely reported. The nerve agent VX is not found in any of the identification sets scheduled for disposal at Rocky Mountain Arsenal, but the nerve agent GB is one of the components of the chemical agent identification and training sets (CAITS). Since the CAIT set is not processed through the glove box, the M-8 paper could be used inside the glove box if there are no false indications of agent from other chemicals which may be present, such as chloroform.

B. Decontamination Tests.

All the tests reported in this section were performed in a laboratory fume hood through which airflow was maintained at a face velocity of approximately 150 feet per minute. As a result, varying rates of evaporation of lewisite, chloropicrin, and mustard were experienced at 75° to 85°F. In a preliminary test, a measured quantity of neat mustard was applied to a surface, was allowed to stand for 5 minutes, and was rinsed off. At temperatures in the 72° to 78°F range, approximately 50 wt % of the mustard was recovered. But at 60° to 68°F, nearly 100 wt % was recovered. These results assured that there would be some measurable agent remaining on the samples even if the evaporation factor were considered.

The results of the decontamination tests with lewisite are presented in table 6. Lewisite discolored the painted surfaces and was assumed to have reacted with the paint. This created no problem for the cellosolve/sodium hydroxide solution because it removed the paint, as well as the agent, during the tests. When working with neat lewisite or dilutions of lewisite in hexane above

Table 6. Chromatograph Response to Lewisite

Surface	Amount applied	Decontaminating condition	Column temperature	Retention time	Peak area
	μℓ		°C	min	
Mild steel plate (unpainted)	5	Control. No decontaminant.	135	2.15 2.15	2631 2950
	5	Applied decontaminant, waited 5 minutes; wiped; then swabbed and wiped two more times.	135	2.15 2.15 2.15 2.15	0 0 0 0
Mild steel plate (painted)	5	Control. No decontaminant.	135	2.17 2.19 2.19	632 1153 53*
	5	Applied decontaminant, waited 5 minutes; wiped; then swabbed and wiped two more times.	135	2.19 2.19 2.19 2.19	0 0 0 0
Stainless steel plate	5	Control. No decontaminant.	135	2.07 2.07	2268 3115
	5	Applied decontaminant, waited 5 minutes; wiped; then swabbed and wiped two more times.	135	2.07 2.07 2.07	0 0 0
Lead	5	Control. No decontaminant.	135	2.15 2.18	14690 14780
	5	Applied decontaminant, waited 5 minutes; wiped; then swabbed and wiped two more times.	135	2.15 2.15 2.15 2.15	0 0 0 0
Polyurethane-coated concrete (9924 A276)	5	Control. No decontaminant.	135	2.17 2.15	8436 7612
	5	Applied decontaminant, waited 5 minutes; wiped; then swabbed and wiped two more times	135	2.16 2.16 2.16 2.16	0 0 0 0
	5	Decontaminated with commercial bleach. Applied and wiped three times. No waiting period.	135	2.16 2.16 2.16 21.6	0 0 0 0

*High evaporation rate.

200 ppm, the sample syringe had to be rinsed thoroughly after each injection. This was necessary to prevent a build-up of contamination of lewisite between samples and to prevent the stainless steel syringe from becoming inoperable after two to three injections.

The high-gloss finish of the polyurethane-coated concrete made it difficult to uniformly distribute the agent on the surface. Instead of forming a layer on the material, the agent dispersed into several beads in the same manner as water on a waxed surface. This made the agent relatively easy to wipe clean, both initially and after the decontaminating solution was applied. Care should be taken when decontaminating with the bleach solution because it also beaded on the polyurethane surface. Since the bleach solution relies heavily on the contact between the sodium hypochlorite and the agent, some difficulty may be experienced in mixing the agent and bleach adequately.

From the results presented in table 6, it is clear that the cellosolve/sodium hydroxide solution is adequate for decontaminating all the surfaces that were tested. No agent was detected (less than 20 to 30 ppm) after decontamination of any of the materials. In addition, decontamination of the polyurethane-coated concrete with commercial bleach [5% to 6% (w/v) sodium hypochlorite] was found to be just as effective as the cellosolve/sodium hydroxide decontamination.

The results of the decontamination tests with chloropicrin are presented in table 7. Beading of the chloropicrin on the polyurethane coating was also experienced in these tests. As with the lewisite, the agent was easily removed before and after the decontaminant was applied. Again, no agent was detected (less than 5 to 8 ppm) after the materials were decontaminated. The commercial bleach removed the agent as well as the cellosolve/sodium hydroxide solution when tested on the polyurethane coating.

The only other agent used in these studies was neat mustard. In addition to the types of tests performed with lewisite and chloropicrin, mustard was used to optimize the decontamination procedures. The results of all the mustard decontamination tests are present in table 8. As noted in the third item of table 8, a detectable quantity of agent remained on the stainless steel plate which was decontaminated one time with the cellosolve/sodium hydroxide solution and immediately wiped and rinsed. The concentration of agent was estimated to be approximately 5 to 7 ppm. In the next test, a single application was made and allowed to sit for 5 minutes before it was wiped and rinsed. Since no mustard was detected (less than 1 ppm), this procedure is considered to have the minimum requirements to insure complete decontamination.

A similar approach was taken with mustard on the polyurethane-coated concrete (item 6, table 8). In this case, the 5-minute waiting period after the decontamination application was not sufficient. This may have resulted from a lower than normal (60° to 70°F) room temperature which was experienced during this time because of a heater problem. Nevertheless, no agent was detected (less than 1 ppm) after a 7-minute waiting period. No further optimization tests were performed. After these tests, only the recommended procedure (section II.B.4.) was used. No agent was detected while the recommended procedure on the six different materials was being used. Again, the commercial bleach was an adequate decontaminant for the polyurethane coating.

Table 7. Chromatograph Response to Chloropicrin

Surface	Amount applied	Decontaminating condition	Column temperature	Retention time	Peak area
	μℓ		°C	min	
Mild steel plate (unpainted)	5	Control. No decontaminant.	90	1.67	12320
				1.67	10280
	5	Applied decontaminant and wiped three times.	90	1.67	0
				1.67	0
				1.67	0
				1.67	0
Mild steel plate (painted)	5	Control. No decontaminant.	90	1.67	9630
				1.67	10740
		Applied decontaminant and wiped three times.	90	1.67	0
				1.67	0
				1.67	0
				1.67	0
Stainless steel plate	5	Control. No decontaminant.	90	1.67	2937
				1.67	2810
		Applied decontaminant and wiped three times.	90	1.67	0
				1.67	0
				1.67	0
Lead	5	Control. No decontaminant.	90	1.67	5262
				1.65	5082
	5	Applied decontaminant and wiped three times.	90	1.66	0
				1.66	0
				1.66	0
				1.66	0
Polyurethane-coated concrete (9924 A276)	5	Control. No decontaminant.	85	2.11	15970
				2.09	13790
	5	Control. No decontaminant.	85	2.12	20670
				2.11	20620
	5	Applied decontaminant and wiped three times.	85	2.12	0
				2.12	0
				2.12	0
				2.12	0
	5	Decontaminated with commercial bleach. Applied and wiped three times.	85	2.10	0
				2.10	0
				2.10	0
				2.10	0

Table 8. Chromatograph Response to Mustard

Surface	Amount applied	Decontaminating condition	Column temperature	Retention time	Peak area
	μℓ		°C	min	
Mild steel plate (unpainted)	2	Control. No decontaminant.	150	2.25 2.25	34820 37000
	2	Applied decontaminant; waited 10 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25	0 0
	2	Applied decontaminant; waited 5 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25	0 0
Mild steel plate (painted)	2	Control. No decontaminant.	150	2.26 2.25 2.26	6724 7322 6616
	2	Applied decontaminant; waited 10 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25 2.25	0 0 0
	2	Applied decontaminant; waited 5 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25 2.25	0 0 0
Stainless steel plate	1	Control. No decontaminant; 5-minute exposure.	150	2.13 2.13	13860 14120
	1	Control. No decontaminant; 10-minute exposure.	150	2.13 2.13	4513 4847
	1	Applied decontaminant. Wiped and rinsed immediately.	150	2.24 2.25 2.24 2.24	1339 1309 1050 1357
	1	Applied decontaminant; waited 10 minutes; wiped and rinsed.	150	2.24 2.24 2.24	0 0 0
	1	Applied decontaminant; waited 5 minutes; wiped and rinsed.	150	2.24 2.24 2.24	0 0 0
		Standard 75 ppm HD/hexane direct injection.	150	2.24	16620
Lead	2	Control. No decontaminant.	150	2.27 2.25 2.26	32100 33060 32930
	2	Applied decontaminant; waited 15 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25 2.25	0 0 0

Table 8. (Continued)

Surface	Amount applied	Decontaminating condition	Column temperature	Retention time	Peak area
	μℓ		°C	min	
Lead (continued)	2	Applied decontaminant; waited 10 minutes; wiped; then swabbed and wiped two times more.	150	2.25 2.25 2.25	0 0 0
	2	Applied decontaminant; waited 5 minutes after initial decontamination.	150	2.25 2.25 2.25	0 0 0
Polyurethane-coated concrete (9924 A276)	1	Control. No decontaminant.	150	2.19 2.19 2.19 2.19	16870 23280 25720 25610
	NOTE:	Room temperature 60° to 70°F			
	1	Applied decontaminant. No wait. Wiped and rinsed immediately.	150	2.19 2.19 2.08	571 513 548
	1	Applied decontaminant; waited 5 minutes; wiped and rinsed once.	150	2.18 2.18 2.18	250 208 199
	1	Applied decontaminant; waited 10 minutes; wiped and rinsed once.	150	2.18 2.18 2.18	0 0 0
Polyurethane-coated concrete (9924 A276)	2	Control. No decontaminant.	150	2.24 2.24 2.25 2.25	47140 44180 43570 40690
	2	Applied decontaminant; waited 5 minutes; wiped and rinsed once.	150	2.25 2.24 2.25	322 256 190
	NOTE:	Room temperature 60° to 70°F		2.26	262
	2	Applied decontaminant; waited 10 minutes; wiped and rinsed once.	150	2.25 2.25 2.25	0 0 0
	2	Applied decontaminant; waited 7 minutes; wiped and rinsed once.	150	2.25 2.25 2.25	0 0 0
	2	Decontamination with commercial bleach. Applied and wiped three times.	150	2.26 2.26	0 0

IV. CONCLUSIONS.

A decontaminating solution consisting of 30 volume parts of a 50% (w/w) aqueous sodium hydroxide solution and 70 volume parts of methyl cellosolve meets the requirements established for a decontaminating solution for use in the disassembly glove box. The recommended procedure for using this decontaminating solution has been shown to be effective and consists of wiping the agent from the surface with paper towels, swabbing the contaminated surface with the decontaminant, waiting 5 minutes, wiping the decontaminant off with paper towels, and swabbing and wiping the surface two more times with no waiting period between them.

To prevent a build-up of pressure, a solution of spent decontaminating solution must be stored in an adequately vented container. Also, since the decontaminating solution is a flammable material (open-cup flash point: 155°F), it must be stored in the proper containers and under the appropriate conditions established for flammable materials (i.e., away from a source of ignition).

While in storage, the decontaminating solution must be protected from carbon dioxide in the air. The sodium hydroxide will react readily with the carbon dioxide to form sodium carbonate. This will reduce the effectiveness of the decontaminating solution.

The M-8 detection paper can be used as the method by which complete decontamination is determined if there are no false indications of agents from other chemicals which may be present in the glove box. Also, only small batches (5 or 6 days' supply) of decontaminating solution should be made at one time to insure the integrity of the solution in the absence of an analytical method.

APPENDIX A

PHYSICAL AND CHEMICAL COMPATIBILITY OF DECONTAMINANTS AND AGENTS

1. Aqueous Sodium Hydroxide.

This solution forms a heterogeneous (2 phase) system when combined with neat mustard, 5% (v/v) mustard in chloroform, 5% (v/v) lewisite in chloroform, 10% (v/v) nitrogen mustard in chloroform, or 50% (v/v) chloropicrin in chloroform. In the agent-chloroform mixtures, the agent will in all cases be partitioned preferentially into the chloroform phase. The reaction of sodium hydroxide with mustard, chloropicrin, or chloroform is very slow.

2. Alcoholic Sodium Hydroxide.

This decontaminant is miscible (homogeneous) with neat mustard, 5% (v/v) mustard in chloroform, 5% (v/v) lewisite in chloroform, 10% (v/v) nitrogen mustard in chloroform. The reaction with neat mustard is very slow ($t_{1/2}$ = 11 hours at 25°C). Similarly, nitrogen mustard is expected to react slowly. The reaction of sodium hydroxide and chloroform is also slow at ambient conditions with the evolution of carbon monoxide. Lewisite is known to react well with sodium hydroxide whenever a surfactant such as hexadecyltrimethylammoniumbromide is used. Without the surfactant, 460 ppm of lewisite was remaining in a mixture after 19 hours.* No information is available on the decontamination of chloropicrin.

3. DS-2 Decontaminating Agent.

DS-2 consists of 2% (w/w) sodium hydroxide, 28% (w/w) methyl cellosolve, and 70% (w/w) diethylenetriamine. DS-2 is miscible with neat mustard, 5% (v/v) mustard in chloroform, 5% (v/v) lewisite in chloroform, and 10% (v/v) nitrogen mustard in chloroform. Although neat mustard and nitrogen mustard react rapidly with the sodium hydroxide in DS-2, the concentration of sodium hydroxide is so low that a large ratio (50:1) of decontaminant to agent will be required. Sodium chloride will be precipitated in the reaction. Lewisite can also be decontaminated with DS-2. With a flash point of 148°F, DS-2 is considered flammable. No information is available on the decontamination of chloropicrin.

4. DANC Solution.

DANC solution consists of 6.25% (w/v) RH-195 in acetylene tetrachloride. RH-195 is 1,3-dichloro-5,5-dimethylhydantoin and is an effective decontaminant for arsenicals if sufficient time is allowed for it to react. Acetylene tetrachloride is probably one of the most toxic chlorinated organic solvents known. It is about 10 times as toxic as carbon tetrachloride. Less than 20 drops ingested can cause death. Sufficient DANC solution will react completely with mustard in approximately 30 minutes. DANC will also decontaminate lewisite and nitrogen mustard, but no specific rate data was found for these and no information was found for chloropicrin. Finally, the DANC solution is considered highly corrosive.

*Rescigno, Nicholas J., and Duggan, Michael L. ARCSL-CR-77036. Demilitarization/Disposal of Obsolete Identification and Training Sets. p 72. August 1977.

5. Supertropical Bleach (STB).

Supertropical bleach is actually calcium hypochlorite. As an aqueous slurry, STB is not miscible with mustard, nitrogen mustard, or lewisite. The two-phase reaction between STB and mustard results in a large release of heat and is very difficult to control. Dry STB and mustard react violently. Chlorine is liberated in both types of reactions as well as in storage. Lewisite reacts with dry STB with the liberation of chlorine. STB is also considered highly corrosive.

6. High-Test Hypochlorite (HTH).

High-test hypochlorite has the same characteristics as the supertropical bleach except that it has approximately twice the quantity of available chlorine.

7. Monoethanolamine (MEA).

Monoethanolamine is miscible with mustard, lewisite, nitrogen mustard, and chloropicrin. The reaction with neat mustard is slow ($t_{1/2}$ = 5.35 hours at 25°C) in a 10:1 (v/v) ratio of MEA to mustard. The reaction is much slower ($t_{1/2}$ = 17.5 hours at 25°C) when the mustard is combined with chloroform. The reaction of lewisite when in a chloroform solution occurs in two steps. The first step (less than 1 second) removes the two chlorine atoms attached to the arsenic atom. The second reaction, in which the third chlorine atom is removed and acetylene is generated, is a slow reaction. The kinetic data on the secondary reaction is incomplete. The reaction with nitrogen mustard is much faster than the other agents ($t_{1/2}$ = 35 minutes at 25°C). And chloropicrin is relatively fast with a half life ($t_{1/2}$) of 9.3 minutes at 34°C. Chloroform will react rapidly with MEA at elevated temperatures.

APPENDIX B

PROPOSED HANDLING AND USE OF DECONTAMINATING SOLUTION FOR IDENTIFICATION SETS DEMILITARIZATION

This appendix to the basic report was requested by the project engineers for demilitarization of identification (ID) sets to give definite information and guidelines toward writing operating SOP's. This appendix is essentially a statement of a concept of usage and may vary from the scenario of actual use.

Concept of Usage. A concept of usage for the proposed sodium hydroxide/methylcellosolve/water decontaminating solution is provided. Comments are also given on mixing, activity verification, and safety. In addition, comments on the use, activity verification, and safety for household bleach (5 wt % to 5.25 wt % sodium hypochlorite) are given.

a. How to Mix Caustic Decontaminating Solution.

(1) The container to hold the decontaminating solution must be steel or plastic as required to hold strong sodium hydroxide (aluminum, magnesium, and glass containers are absolutely unacceptable).

(2) The solution should be made in small or moderate batches to be used within 1 work week to insure effectiveness of the decontaminating properties. Any solution remaining after 1 work week should be discarded. Seventy volume parts of methylcellosolve are to be added to the container tank and 30 volume parts of 50% sodium hydroxide are added. The mixture should be stirred several minutes until homogeneous. The heat of dilution generated will be minimal and is expected to be of little or no consequence. It must be PROTECTED from the CARBON DIOXIDE (CO_2) in the air to maintain its effectiveness.

b. When and How to Use.

(1) Caustic/methylcellosolve/water decontamination. The decontamination solution effectiveness is the result of two actions. It dissolves and physically removes the chemical agent from the surfaces to be decontaminated and also chemically neutralizes the agent. After a steel pig has been emptied, the flange face of the pig and the inside of the cover should be decontaminated before the cover plate is reassembled onto the pig. The flange area and the outer surface of the cover of the closed pig, including the bolts and nuts, should also be decontaminated as described below.

(a) The decontaminating solution is to be applied generously to thoroughly wet all potentially contaminated surfaces. The application of the decontaminant should be repeated two or more times (a minimum of three generous applications). The gross excess of the decontaminating solution should be allowed to drain off, with a residual coating remaining on the pig. The residual layer will trap and neutralize toxic chemical vapors which could arise from chemical agent trapped in cracks and crevices of the metal surfaces. This residual decontaminating layer will also be very corrosive to human skin; therefore, the decontaminated pigs must be handled with rubber apron and gloves.

(b) Used decontaminating solution should be collected in a drum that should have a vent or a loose-fitting cover. The slow reaction of chloroform contained in ID sets and the decontaminating solution will release gas and will cause an undesirable pressure build-up in a tightly closed container.

CAUTION: This solution is combustible and must not be used near flames or other sources of ignition. It must be used *only* where adequate airflow is provided to prevent an explosive accumulation of vapor. HANDLE the solution as if it were a strong SODIUM HYDROXIDE (CAUSTIC).

(2) Bleach.

(a) Commercial household bleach (5 wt % to 5.25 wt % sodium hypochlorite) in 1-gallon containers should be used to decontaminate concrete floor areas. It is not envisioned that a large or massive spill should occur outside of the glove box. The contaminated area of the spill should be covered with a generous layer of bleach. The bleach over the area will be stirred with a broom or other utensil to aid in the complete decontamination. A generous layer of bleach should be left on the area for a minimum of 1 hour.

(b) Bleach is corrosive to stainless steel and, if used on this metal, it should be flushed down as soon as possible. Before using bleach, see paragraph d. (below) on safety.

c. Activity of Decontaminating Solution.

(1) Caustic/methylcellosolve/water decontamination. The color change from light to dark is to be ignored. This solution must be protected from exposure to the atmosphere to preclude pickup of water and carbon dioxide (CO_2). The unused solution should be discarded at the end of the working week. The solution should be discarded if the formation of a soft gel hampers the ready application of the decontaminating solution. The sodium hydroxide content should be not less than 12.0 wt/v %. The sodium hydroxide content may be determined by the following procedure.

Determination of sodium hydroxide content.

Reagents

Hydrochloric acid 0.1 N standardized
Distilled water
Phenophthalein indicator 1% in ethanol

Pipet a 1.0-ml sample of the decontaminating solution into a 125-ml Erlenmeyer flask containing 10 ml of water. Add 6 drops of phenolphthalein indicator and titrate with standardized 0.1 N hydrochloric acid to the colorless endpoint of phenolphthalein.

Calculation:

$$\frac{A \times N \times 40 \times 100}{V \times 1000} = \% \text{ NaOH}$$

where

A = ml standardized hydrochloric acid

N = normality of hydrochloric acid

V = ml of sample

(2) Bleach. The bleach solution is considered to have an adequate reactivity if the sodium hypochlorite content is not less than 4.0% wt/wt. (Household bleach is normally labeled 5% wt/wt to 5.25% wt/wt sodium hypochlorite.) The sodium hypochlorite (NaOCl) content will be determined by the following procedure:

Determination of NaOCl content.

Reagents

Distilled water

Potassium iodide, ACS specifications

Concentrated sulfuric acid diluted 1 to 1 with distilled water

(Caution: Add acid slowly to water; solution gets very hot)

0.1 N sodium thiosulfate, standardized

Weigh a 1.0-gm sample to the nearest 0.1 mg in a tared glass ampoule. Place the ampoule with weighed sample into a 500-ml iodine flask containing 50 ml of distilled water. Break the ampoule with a glass rod, wash down the rod, and remove from the flask. Immediately add 10 ml of 1:1 sulfuric and 2 gm potassium iodide, swirl to mix, stopper, and seal the flask with water. Allow the flask to sit in the dark 15 minutes. Remove the flask from the dark, remove the stopper, and rinse the stopper with water into the original flask. Titrate with standardized 0.1 N sodium thiosulfate to the colorless endpoint.

Calculation:

$$\frac{A \times N \times 74.5 \times 100}{W \times 2 \times 1000} = \% \text{ NaOCl}$$

where

A = ml sodium thiosulfate

N = normality of sodium thiosulfate

W = weight of sample in grams

d. Safe Handling of Decontaminating Solutions.

(1) Bleach. Bleach (sodium hypochlorite 5.25 wt % aqueous solution, household) is corrosive to the skin and eyes. Precautions must be taken when handling bleach to preclude splashing on the skin and especially into the eyes. If bleach is splashed on the skin or clothing, it must be removed immediately by flushing with water. If bleach is splashed into the eyes, the eyes must be flushed with clean water and medical help obtained. Bleach is incompatible with and must *NOT* be mixed with acid or ammonia due to the potential vigorous reaction and the toxic fumes that are released.

(2) Caustic/methylcellosolve decontamination. The caustic/methylcellosolve decontamination solution is essentially a strong sodium hydroxide solution and must be respected and handled accordingly. Sodium hydroxide (lye, caustic) is very corrosive to the skin and especially to the eyes. Sodium hydroxide must be flushed from the skin or eyes with copious amounts of water. Medical help is absolutely required for caustic in the eyes. Rubber gloves, apron, and a face shield are required when using the decontaminant solution outside of the glove box. In addition to the corrosiveness of the caustic, this solution contains methylcellosolve which is flammable. The decontaminating solution must *NOT* be used near flames or other sources of ignition. It also *must* be used with an adequate airflow to prevent the accumulation of an explosive vapor concentration.

APPENDIX C

MATERIAL SAFETY DATA SHEET (Methyl Cellosolve)*

Data obtained from Union Carbide "Material Safety Data Sheet" for methyl cellosolve and Union Carbide technical bulletin "Glycol Ethers."

CHEMICAL NAME:	METHYL CELLOSOLVE
SYNONYMS:	2-Methoxyethanol; Ethylene Glycol Monomethyl Ether
CHEMICAL FAMILY:	Glycol Ethers
FORMULA:	$CH_3OC_2H_4OH$
MOLECULAR WEIGHT:	76.10
TRADE NAME AND SYNONYMS:	Methyl CELLOSOLVE

I. PHYSICAL DATA

BOILING POINT, 760 mmHg	124.5°C (256.1°F)	FREEZING POINT	-85.1°C
SPECIFIC GRAVITY (H_2O = 1)	0.9663 at 20/20°C	VAPOR PRESSURE AT 20°C	6 mmHg
VAPOR DENSITY (air = 1)	2.62	SOLUBILITY IN WATER, % by wt at 20°C	Complete
PERCENT VOLATILES BY VOLUME	100	EVAPORATION RATE (Butyl Acetate = 1)	0.47
APPEARANCE AND ODOR	Water-white liquid; mild and nonresidual odor		

II. HAZARDOUS INGREDIENTS

MATERIAL	%	TLV (Units)
2-Methoxyethanol	~100	25 ppm (Skin) (ACGIH) (OSHA)
(See Sections III through VIII)		

III. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (test method)	103°F, Tag closed cup	AUTOIGNITION TEMPERATURE	551°F		
FLAMMABLE LIMITS IN AIR, % by volume		LOWER	2.5	UPPER	19.8
EXTINGUISHING MEDIA	Use carbon dioxide or dry chemical for small fires. Use alcohol foam or water for large fires.				
SPECIAL FIRE FIGHTING PROCEDURES	None				
UNUSUAL FIRE AND EXPLOSION HAZARDS	None				

IV. HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE	25 ppm – ACGIH (1975) and OSHA – CFR 29 § 1000 Table G 1
EFFECTS OF OVEREXPOSURE	All glycol ethers have narcotic properties. Brief exposure to vapors will not be harmful. Mild exposure will cause dizziness and moderate irritation to the eyes, nose, and throat. Removal to fresh air results in quick relief from this irritation. Prolonged and repeated exposure to high concentrations will cause drowsiness progressing to dizziness, nausea, vomiting, and loss of consciousness. If a dose is large enough or administered over a long period of time, injury to the kidneys and the liver may result. While systemic injury has been demonstrated in experimental animals, it has not yet been reported as occurring in humans working with glycol ethers. Methyl cellosolve is reported to have caused human systemic illness. Where methyl cellosolve was heated to provide high concentrations, several workers became ill after many weeks of exposure. The illness consisted of personality changes, mental dullness, anemia, continuous drowsiness, loss of appetite, weakness, and weight loss. Recovery occurred several months after exposure was terminated. In another group, the symptoms were much the same, but instead of mental dullness the employees were semi-maniacal and were first thought to have a mental illness. Again, recovery occurred in several months following removal from exposure. In all situations where human illness occurred, heat had been applied to increase the volatility of methyl cellosolve. No cases of illness have been reported from uses where the solvent was not heated. Like all solvent materials, prolonged or repeated skin contact will remove skin waxes and oils. Recovery from this irritation is prompt after the excessive contact is terminated.
EMERGENCY AND FIRST AID PROCEDURES	Flush skin and eye contact with water. If inhaled, remove to fresh air. If not breathing, give artificial respiration. Give oxygen if breathing is difficult. Call a physician.

V. REACTIVITY DATA

STABILITY			
UNSTABLE	STABLE	CONDITIONS TO AVOID	None
–	✓		

INCOMPATIBILITY (materials to avoid)	None
HAZARDOUS DECOMPOSITION PRODUCTS	Thermal decomposition or burning may produce carbon monoxide and/or carbon dioxide.

HAZARDOUS POLYMERIZATION			
May Occur	Will not Occur	CONDITIONS TO AVOID	None
–	✓		

VI. SPILL OR LEAK PROCEDURES

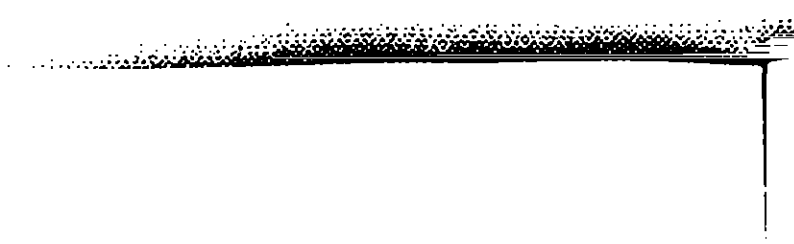
STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	Small spills should be flushed with large quantities of water. Larger spills should be collected for disposal.
WASTE DISPOSAL METHOD	Incinerate in a furnace where permitted under appropriate Federal, State, and local regulations.

VII. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (specify type)		Supplied-air respirator for high concentrations.		
VENTILATION	LOCAL EXHAUST	Preferable	SPECIAL	–
	MECHANICAL (general)	Acceptable	OTHER	–
PROTECTIVE GLOVES		Plastic gloves	EYE PROTECTION	Safety goggles
OTHER PROTECTIVE EQUIPMENT		Safety shower and eye bath		

VIII. SPECIAL PRECAUTIONS

PRECAUTIONARY LABELING	**METHYL CELLOSOLVE®** **Ethylene Glycol Monomethyl Ether** **WARNING! HARMFUL IF INHALED** **COMBUSTIBLE** **Avoid breathing vapor.** **Keep away from heat and open flame.** **Keep container closed.** **Use with adequate ventilation.** **FIRST AID: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.** **FOR INDUSTRY USE ONLY**
OTHER HANDLING AND STORAGE CONDITIONS	Store glycol ethers in carbon steel for most applications. Where trace iron contamination or slight discoloration are critical, consider lined steel or stainless steel tanks. Methyl cellosolve should not be stored or handled in aluminum. Copper alloys cause discoloration of the glycol ethers in the presence of air or dissolved oxygen. Most glycol ethers do not present a significant flammability hazard at normal storage. They have relatively low vapor pressures. The most volatile are PROPASOL Solvent M and methyl cellosolve, which have flash points of 91° and 103°F, respectively. Glycol ethers are not particularly hygroscopic. Tanks storing them can often be vented directly to the atmosphere. Methyl cellosolve has a relatively low viscosity and low freezing point. Heated storage is not required. Piping can be made of the same material as that of the storage tank. Reinforced plastic piping may be suitable and is worthy of consideration if iron contamination or slight discoloration are critical. A centrifugal pump is suitable for transfer service. Butyl rubber and asbestos can be used for gaskets and packing.



CH

SA

AU

BIC

CB

DE

EN

MU

PH

RE

SY

DE

Ad
De

Ca
Ale

DISTRIBUTION LIST 4

Names	Copies
CHEMICAL SYSTEMS LABORATORY	
SAFETY OFFICE	
Attn: DRDAR-CLF	1
AUTHOR'S COPIES: Research Division	5
Munitions Division	5
BIOMEDICAL LABORATORY	
Attn: DRDAR-CLL-B	1
Attn: DRDAR-CLL-M	1
Attn: DRDAR-CLL-MC	1
Attn: DRDAR-CLL-V	1
CB DETECTION & ALARMS DIVISION	
Attn: DRDAR-CLC-C	1
Attn: DRDAR-CLC-E	1
DEVELOPMENTAL SUPPORT DIVISION	
Attn: DRDAR-CLJ-R	3
Attn: DRDAR-CLJ-L	3
Attn: DRDAR-CLJ-M	1
Attn: DRDAR-CLJ-P	1
ENVIRONMENTAL TECHNOLOGY DIVISION	
Attn: DRDAR-CLT-D	4
MUNITIONS DIVISION	
Attn: DRDAR-CLN	2
PHYSICAL PROTECTION DIVISION	
Attn: DRDAR-CLW	2
Attn: DRDAR-CLW-C	1
Attn: DRDAR-CLW-P	1
Attn: DRDAR-CLW-E	1
RESEARCH DIVISION	
Attn: DRDAR-CLB	1
Attn: DRDAR-CLB-B	1
Attn: DRDAR-CLB-C	1
Attn: DRDAR-CLB-P	1
Attn: DRDAR-CLB-R	1
Attn: DRDAR-CLB-T	1
Attn: DRDAR-CLB-TE	1
SYSTEMS DEVELOPMENT DIVISION	
Attn: DRDAR-CLY-A	1
Attn: DRDAR-CLY-L	1
Attn: DRDAR-CLY-R	1
Attn: DRDAR-CLY-T	1
DEPARTMENT OF DEFENSE	
Administrator Defense Documentation Center Attn: Document Processing Division (DDC-DD) Cameron Station Alexandria, VA 22314	2
Director Defense Intelligence Agency Attn: DB-4G1 Washington, DC 20301	1
DEPARTMENT OF THE ARMY	
HQDA (DAMO-SSC) WASH DC 20310	1
Director Defense Civil Preparedness Agency Attn: PO(DC) Washington, DC 20301	1
CINCUSAREUR Attn: AEAGC-RSI APO New York 09403	1
Deputy Chief of Staff for Research, Development & Acquisition	
Attn: DAMA-CSM-CM	1
Attn: DAMA-ARZ-D Washington, DC 20310	1
US Army Research and Standardization Group (Europe) Attn: Chief, Chemistry Branch Box 65, FPO New York 09510	1
HQDA (DAMI-FIT) WASH, DC 20310	1
Commander HQ US Army Medical Command, Europe Attn: AEMPM APO New York 09403	1
US ARMY HEALTH SERVICE COMMAND	
Superintendent Academy of Health Sciences US Army	
Attn: HSA-CDC	1
Attn: HSA-IHE Fort Sam Houston, TX 78234	1
US ARMY MATERIEL DEVELOPMENT AND READINESS COMMAND	
Commander US Army Materiel Development and Readiness Command	
Attn: DRCLDC	1
Attn: DRCSF-P 5001 Eisenhower Ave Alexandria, VA 22333	1

DISTRIBUTION LIST 4 (Contd)

Names	Copies
Commander	
US Army Toxic and Hazardous Materials Agency	
Attn: DRXTH-TS	2
Attn: DRXTH-CD	1
Attn: DRXTH-CD-S	12
Aberdeen Proving Ground, MD 21010	
Human Engineering Laboratory HFE Detachment	
Attn: DRXHE-EA	1
Building E3220	
Aberdeen Proving Ground, MD 21010	
Commander	
US Army Foreign Science & Technology Center	
Attn: DRXST-MT2	1
220 Seventh St., NE	
Charlottesville, VA 22901	
US Army Materiel Systems Analysis Activity	
Attn: DRXSY-MP	1
Attn: DRXSY-T (Mr. Kaste)	1
Aberdeen Proving Ground, MD 21005	
Commander	
US Army Missile Research and Development Command	
Redstone Scientific Information Center	
Attn: DRDMI-TBD	1
Redstone Arsenal, AL 35809	
Director	
DARCOM Field Safety Activity	
Attn: DRXOS-C	1
Charlestown, IN 47111	
US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND	
Commander	
US Army Armament Research and Development Command	
Attn: DRDAR-AC	1
Attn: DRDAR-LCE-M	1
Attn: DRDAR-LCH	1
Attn: DRDAR-LCN	1
Attn: DRDAR-LCU	1
Attn: DRDAR-SER	1
Attn: DRDAR-TSS	2
Attn: DRCPM-CAWS-WP	1
Dover, NJ 07801	
Director	
Ballistic Research Laboratory	
Attn: DRDAR-TSB-S	1
Building 305	
Aberdeen Proving Ground, MD 21005	
CDR, APG	
USA ARRADCOM	
Attn: DRDAR-GCL	1
Aberdeen Proving Ground, MD 21010	
Commander	
USA Technical Detachment	
US Naval EOD Facility	1
Indian Head, MD 20640	

Names	Copies
US ARMY ARMAMENT MATERIEL READINESS COMMAND	
Commander	
US Army Armament Materiel Readiness Command	
Attn: DRSAR-ASN	1
Attn: DRSAR-IRB	1
Attn: DRSAR-PDM	1
Attn: DRSAR-PE	1
Attn: DRSAR-SF	1
Attn: DRSAR-SR	1
Rock Island, IL 61299	
CDR, APG	
USA ARRCOM	
Attn: DRSAR-MAS-C	1
Attn: SARTE	1
Aberdeen Proving Ground, MD 21010	
Commander	
US Army Dugway Proving Ground	
Attn: Technical Library, Docu Sect	1
Dugway, UT 84022	
Commander	
Rocky Mountain Arsenal	
Attn: SARRM-QA	1
Attn: SARRM-MD	1
Commerce City, CO 80022	
Commander	
Pine Bluff Arsenal	
Attn: SARPB-ETA	1
Pine Bluff, AR 71611	
US ARMY TRAINING & DOCTRINE COMMAND	
Commandant	
US Army Infantry School	
Attn: NBC Division	1
Fort Benning, GA 31905	
Commandant	
US Army Missile & Munitions Center & School	
Attn: ATSK-CD-MD	1
Attn: ATSK-DT-MU-EOD	1
Redstone Arsenal, AL 35809	
Commandant	
US Army Military Police School/Training Center	
Attn: ATZN-CDM	1
Attn: ATZN-TDP-C	1
Fort McClellan, AL 36205	
Commander	
US Army Infantry Center	
Attn: ATSH-CD-MS-C	1
Fort Benning, GA 31905	

DISTRIBUTION LIST 4 (Contd)

Names	Copies
Commander US Army Ordnance & Chemical Center & School Attn: ATSL-CL-CD Aberdeen Proving Ground, MD 21005	1
US ARMY TEST & EVALUATION COMMAND	
Commander US Army Test & Evaluation Command Attn: DRSTE-FA Aberdeen Proving Ground, MD 21005	1
President US Army Infantry Board Attn: ATZB-IB-MI Fort Benning, GA 31905	1
DEPARTMENT OF THE NAVY	
Chief of Naval Research Attn: Code 443 800 N. Quincy Street Arlington, VA 22217	1
Commander Naval Facilities Engineering Command Attn: Code 03 200 Stovall Street Alexandria, VA 22332	1
Commander Naval Explosive Ordnance Disposal Facility Attn: Army Chemical Officer, Code 604 Indian Head, MD 20640	1
Commander Nuclear Weapons Training Group, Atlantic Naval Air Station Attn: Code 21 Norfolk, VA 23511	1
Chief, Bureau of Medicine & Surgery Department of the Navy Washington, DC 20372	1
Commander Naval Weapons Center Attn: Code 3171 China Lake, CA 93555	1

Names	Copies
US MARINE CORPS	
Director, Development Center Marine Corps Development & Education Command Attn: Fire Power Division Quantico, VA 22134	1
DEPARTMENT OF THE AIR FORCE	
Air University Library Attn: AUL/LSE-8879 Maxwell AFB, AL 36112	1
HQ Foreign Technology Division (AFSC) Attn: PDRR Wright-Patterson AFB, OH 45433	1
Commander Aeronautical Systems Division Attn: ASD/AELD Wright-Patterson AFB, OH 45433	1
HQ, USAF/SGPR Forrestal Bldg WASH DC 20314HQ	1
HQ AFSC/SDAE Andrews AFB, MD 20334	1
HQ AFISC/SEV Norton AFB, CA 92409	1
NORAD Combat Operations Center/DBN Cheyenne Mtn Complex, CO 80914	1
AMREL/MEB Wright-Patterson AFB, OH 45433	1
OUTSIDE AGENCIES	
Battelle, Columbus Laboratories Attn: TACTEC 505 King Avenue Columbus, OH 43201	1
Director of Toxicology National Research Council 2101 Constitution Ave, NW Washington, DC 20418	1
ADDITIONAL ADDRESSEES	
Commander USEUCOM Attn: ECJ5-O/LTC James H. Alley APO, NY 09128	1

DISTRIBUTION LIST 4 (Contd)

Names	Copies
Commander/Director	
Chemical Systems Laboratory	
Attn: DRDAR-CLN-E	1
Attn: DRDAR-CLN-ES	5
Attn: DRDAR-CLN-T	1
Attn: DRDAR-CLB-RA	1
Attn: DRDAR-CLT-D	2
Attn: DRDAR-QAC-D	2
Aberdeen Proving Ground, MD 21010	
Commander	
Armament Concepts Office, Weapon Systems Concepts Team	
Attn: DRDAR-ACW	1
Aberdeen Proving Ground, MD 21010	

Names	Copies
Commander	
Rocky Mountain Arsenal	
Attn: SARRM-QAL	1
Attn: SARRM-FE	1
Attn: SARRM-FEE	1
Attn: SARRM-FEE-M	1
Attn: SARRM-FEO	2
Commerce City, CO 80022	

Background document I, Reference 6

Departments of the Army, Navy, and Air Force, 1990, Potential Military Chemical/Biological Agents and Compounds, Field Manual 3-9, Washington, D.C.

See Preamble, Reference 18

ANNEX B (DESCRIPTION OF AGENTS) TO OPLAN FOR RANGE CLEARANCE OF DPG HAZARDOUS AREAS

I. PURPOSE:

To provide an accurate, concise source of information on the characteristics, hazards and symptoms from exposure to agents that were tested and or disposed of at DPG.

II. AGENT DESCRIPTION:

A. Agent GB and GA:

1. Description: GB is a volatile rapid-acting, lethal nerve agent. When dispersed as large droplets, GB is moderately persistent; when disseminated as an aerosol, it is non-persistent.

2. Hazard: Primary entry into the human body is by vapor absorption through the respiratory tract, although absorption through skin, eyes and ingestion are also likely. The action of the agent, once entry into the body is gained, is through the inactivation of cholinesterase enzyme.

3. Symptoms of exposure:

a. Initial symptoms and mild exposure: Pinpointing of eye pupils (myosis) and dimness of vision (both of which may be absent in cases of skin absorption), running nose, tightness of chest and difficulty in breathing are early symptoms of vapor contamination. Early symptoms of exposure by skin contact may be localized sweating and muscular twitching.

b. Later symptoms of severe exposure: Nausea and possible vomiting, cramps, involuntary defecation and/or urination, headache, drowsiness, coma, convulsions and cessation of breathing.

4. Physical properties of GB:

a. Chemical name: Isopropyl methyl phosphonofluoridate

b. Chemical formula: CH_3 (FPO) OC_3 H_7

c. Molecular weight: 140.00

d. Vapor density (air = 1.00): 4.86

e. Liquid density at 77° F: 1.0998 gm/cc

f. Freezing point: -69° F

g. Boiling point: 297° F

h. Vapor pressure at 77° F: 2.2 mm Hg

i. Color: clear to straw to amber

j. Odor: none

5. Physical properties of GA:

a. Chemical name: Dimethylamino ethorxy-cyanophrosphite oxide

b. Chemical formula: CH_3 CH_3 $N - P(=O) - CN - O - C_5 H_2$

c. Molecular weight: 163.3

d. Vapor density: 5.63

e. Liquid density: 1.073 @25° C

f. Freezing point: -49° to 50° C

g. Boiling point: 246° C

h. Vapor pressure: 0.070 mm Hg @25° C

i. Color: colorless to brownish liquid

j. Odor: faintly fruity; none when pure

B. Agent VX:

1. Description: VX is a rapid acting, lethal nerve agent. The compound is slow to evaporate and is classed as a persistent agent.

2. Hazard: Entry of VX into the body is primarily through skin absorption, although injestion and inhalation of vapor are also possible. The action of VX in the body is by the inactivation of cholinesterase enzyme.

3. Symptoms of exposure: Same as GB and GA (see section II.A.3).

4. Physical properties:

a. Chemical name: O-ethyl S-(2-diisopropylaminoethyl) methyl-phosphonothioate.

b. Chemical formula: $CH_3P(O)\ (OC_2H_5)\ SC_2H_4N(C_3H_7)2$

c. Molecular weight: 267.38

d. Liquid density at 25^o C: 1.008 g/cm^3

e. Vapor pressure at 20^o C: 0.00066mm Hg

f. Freezing point: Below -59.8^o F

g. Boiling point: 572^o F

h. Color: clear to straw

i. Odor: none

j. Flash point: 318.2^o F

k. Volatility: 9.7 mg/m^3 at 68^o F

C. Mustard:

1. Description: Mustards are best described as persistent blister agents. There are three types of mustard currently in munitions:

a. H which is the symbol for mustard prepared by the Levinstein process. This agent contains approximately 25 percent impurities by weight, chiefly sulfur, organo-sulfur-chlorides and polysulfides.

b. HD is [illegible] by washing and vacuum distillation.

c. HT is a mixture of 60 percent HD and 40 percent bis-beta-chlorethyl thioethyl ether, $(C_1C_2H_4SC_2H_4)_2O$. The latter is added to lower the freezing point to 32^o F.

2. Hazard: Mustard is a persistent and powerful blister agent. Both liquid and vapor cause intense inflammation, which may blister the

skin or mucous membrane they touch. HT is less volatile than HD and H has little vapor hazard.

3. Symptoms: The first symptoms of mustard poisoning usually appear within four to six hours. The higher the concentration, the shorter the interval of time between the exposure and the first symptoms. Exposure results in conjunctivitis (inflammation of the eyes); erthema (redness of the skin) which may be followed by blistering or ulceration; and inflammation of the nose, throat, trachea, bronchi, and lung tissue.

4. Physical properties:

a. Chemical name: 2.2'-dichlorodiethylsulfide

b. Chemical Formula: $(ClCH_2CH_2)_2S$

		H	HD
c.	Molecular weight:	175.00	159.08
d.	Vapor density (air=1.0):	5.4	5.4
e.	Liquid density at 68^0 F	1.7 gm/cc	1.27 gm/cc
f.	Freezing point:	41^0 - 57^0 F	58^0 F
g.	Boiling point:	437.7^0 F	442.4^0 F
h.	Vapor pressure at 68^0 C:	0.059mm Hg	0.072mm Hg
i.	Specific gravity	70-75 percent	94-96 percent
j.	Color	amber	amber
k.	Odor	garlic	garlic

5. Physical properties:

a. Chemical name: 2.2'-dichlorodiethylsulfide

b. Chemical formula: $(ClCH_2CH_2)_2S$ HT

c. Molecular weight:

d. Vapor density (air = 1.0): 5.4

e.	Liquid density at 68° F	intermediate
f.	Freezing point:	32° F
g.	Boiling point:	
h.	Vapor pressure at 68° F	.079 mm Hg
i.	Specific gravity	60 percent
j.	Color	amber
k.	Odor	garlic

D. Agent CG (Phosgene)

1. Description: CG is normally a chemical agent with a short duration of effectiveness. The action of the agent is normally delayed, however, exposure to high concentrations may produce immediate effects. CG is a choking agent and the target is the lungs via inhalation.

2. Hazard: Choking agents injure unprotected man chiefly in the respiratory tract, ie, the nose, throat and particularly the lungs. In extreme cases, membranes swell, lungs become filled with liquid and death results from lack of oxygen.

3. Symptoms of exposure:

Phosgene exerts its effects solely on the lungs, and results in damage to the capillaries. It causes seepage of fluid into the air sacs. When a lethal amount of CG is received, the air sacs become so flooded that air is excluded and the victim dies of anoxia (oxygen deficiency). If the amount of CG is less than lethal, and proper care is provided, the watery fluid is reabsorbed, the air cell walls heal, and the patient recoveres. The severity of poisoning cannot be estimated from the immediate symptoms, since the full effect is not usually apparent until three or four hours after exposure. Most deaths occur within 24 hours.

4. Physical properties:

a. Chemical name: Carbonyl Chloride (also Chloroforml chloride)

b. Chemical formula: $COCl_2$

c. Molecular weight: 98.92

d. Vapor density: 4.4

e. Liquid density: 1.42,0°C

f. Freezing point: -104 to 128° C

g. Boiling point: 7.56° C

h. Vapor pressure: 1,173mm Hg, 20° C

i. Volatility: 6.4 x 10^6 mg/m^3 at 20° C

j. Decomposition temperature: 800° C

k. Odor: new-mown hay or grass; green corn

E. Agents AC (hydrogen cyanide) and CK (cyanogen chloride)

1. Description: AC & CK are rapid acting lethal blood agents. These agents are highly volatile and are non-persistent agents. CK has the additional characteristics above AC as follows:

a. It has a choking effect

b. It has a strong irritating effect

c. Causes a slow breathing rate

2. Hazard: Blood agents are absorbed into the body primarily by breathing. They affect body functions through actions on the enzymes cytochrome-oxidase, thus preventing the normal transfer of oxygen from the blood to the body tissues.

3. Symptoms of exposure: Affects the body by causing a marked stimulation of the breathing rate. CK has the opposite effect. Wearing of the protective mask provides adequate protection. In working with CK, care must be taken to periodically check the cannister because the cyanogen chloride will break down the cannister.

4. Physical properties:

a. Chemical name: Hydrogen cyanide

b. Chemical formula: HCN

c. Molecular weight:

d. Vapor density: 0.93

e. Liquid density; 0.697 @10^{o} C

f. Freezing point: -14^{o} C

g. Boiling point: 26^{o} C

h. Vapor pressure: 757mm Hg @26^{o} C

i. Volatility: 37,000 mg/m^{3} @-40^{o} C, 1,075,000 mg/m^{3} @25^{o}C

j. Decomposition temperature: above 65.5^{o} C

k. Odor: similar to peach kernals

5. Physical properties of CK:

a. Chemical name: Cyanogen Chloride

b. Chemical formula: CNCl

c. Molecular weight: 61.48

d. Vapor density: 2.1

e. Liquid density: 1.18, 20^{o} C

f. Freezing point: -7 to -5^{o} C

g. Boiling point: 13^{o} C

h. Vapor pressure: 1,010mm Hg at 20^{o} C

i. Volatility: 6.1 x 10^{6} mg/m^{3} at 25^{o} C

j. Decomposition temperature: above 100^{o} C

k. Odor: Masked by its great irritating and lacrimatory properties.

F. Agent WP (White Phosphorus)

1. Description: White phosphorus may be considered a screening smoke and an incendiary agent. It may be used for obscuration or target destruction.

2. Hazard: The primary hazard of WP to personnel is burning. Such burning heal very slowly. In enclosed spaces, WP may consume the oxygen thus smothering personnel inside. Vapors of WP are poisonous, producing bone decay.

3. Physical properties:

a. Chemical name: White or yellow phosphorus

b. Formula: P_4

c. Molecular weight: 124.11

d. Density of solid: 1.83 @ 20^{o} C

e. Freezing point: 44^{o} C

f. Boiling point: 290^{o} C

g. Odor: like matches.

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

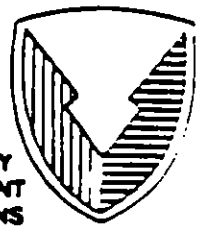
CRDEC-TR-009

SUPPORT FOR THE DELISTING OF DECONTAMINATED LIQUID CHEMICAL SURETY MATERIALS AS LISTED HAZARDOUS WASTE FROM SPECIFIC SOURCES (STATE) MD02 IN COMAR 10.51.02.16-1

H. DuPont Durst, Ph.D.
Emory W. Sarver, Ph.D.
Harvey W. Yurow, Ph.D.
William T. Beaudry, Ph.D.
Patsy A. D'Eramo
Donna M. Jackson
Harry Salem, Ph.D.
John B. Samuel
Linda L. Szafraniec
F. Prescott Ward, Ph.D.
J. Richard Ward, Ph.,D.

RESEARCH DIRECTORATE

November 1988



U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No 0704 0188

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-009	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION CRDEC 6b OFFICE SYMBOL (If applicable) SMCCR-RSC-C	7a NAME OF MONITORING ORGANIZATION
6c ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING/SPONSORING ORGANIZATION CRDEC 8b OFFICE SYMBOL (If applicable) SMCCR-RSC-C	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO: PROJECT NO.: 1L162706 TASK NO: A553F WORK UNIT ACCESSION NO:

11 TITLE (Include Security Classification)
Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD02 in COMAR 10.51.02.16-1

12 PERSONAL AUTHOR(S) Durst, DuPont, H., Ph.D.; Sarver, Emory W., Ph.D.; Yurow, Harvey W., Ph.D.; Beaudry, William T., Ph.D.; D'Eramo, Patsy A.; (continued on reverse)

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 87 Dec TO 88 Feb	1988 November	178

16 SUPPLEMENTARY NOTATION
Prepared for the Office of Environmental Programs, Department of Health and Mental Hygiene, State of Maryland

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
15	02		Surety materials Product Analysis Product Toxicology
07	03		Decontamination Kinetic Analysis Historical Background
			Hydrolysis Thermodynamics (continued on reverse)

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Maryland recently enacted regulations that listed decontaminated residues of certain chemical warfare agents as hazardous wastes. The State would consider delisting if the Army document the effects of its decontamination procedures. Army specialists at U.S. Army Chemical Research, Development and Engineering Center (CRDEC), Aberdeen Proving Ground, MD, have had exhaustive experience in this area since 1918 when chemical agents were first used in combat in World War I. Competence accrued during this 70-year legacy includes destruction of laboratory and training wastes, combat decontamination, and largescale demilitarization of unserviceable and obsolete agent-filled munitions. The facts and circumstances enumerated in this document indicate that current decontamination practices are safe, scientifically valid, and result in the total destruction of agents in question. Several basic issues were addressed. (1) Do theoretical chemical calculations (continued on reverse)

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON	22b TELEPHONE (Include Area Code) (301) 671-2914 22c OFFICE SYMBOL SMCCR-SPS-T

DD Form 1473, JUN 86 Previous editions are obsolete SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

UNCLASSIFIED

12. Personal Author(s) (continued)

Jackson, Donna M.; Salem, Harry, Ph.D.; Samuel, John B.; Szafraniec, Linda L.; Ward, F. Prescott, Ph.D.; and Ward, J. Richard, Ph.D.

18. Subject Terms (continued)

Regulatory background
Decontamination protocols
Nuclear magnetic resonance Analysis

19. Abstract (continued)

support claims that agents plus decontaminants yield products that no longer contain agents? They do. Reaction energies, reaction kinetics, chemical equilibrium, laws of thermodynamics, and other mathematical considerations indicate that A + B do indeed equal C + D. (2) Are older decontamination procedures that used different reagents equivalent to today's protocols and reagents? In most cases, yes. For example, when using hydroxide or sodium carbonate, the reactive decontaminating moiety in both cases is the hydroxyl ion. (3) Do analytical results and toxicological data substantiate complete destruction of chemical agents when decontaminated? Yes. Extensive information accrued since 1918 provides incontrovertible scientific evidence of decontamination efficacy.

EXECUTIVE SUMMARY

Maryland recently enacted regulations that listed decontaminated residues of certain chemical warfare agents as hazardous wastes. Delisting would be considered by the State were the Army to document the efficacy of its decontamination procedures.

Army specialists at Edgewood, MD (Chemical Research, Development & Engineering Center - CRDEC) have had exhaustive experience in this area since 1918 when chemical agents were first used in combat in World War I. Competence accrued during this seventy-year legacy includes destruction of laboratory and training wastes, combat decontamination, and large-scale demilitarization of unserviceable and obsolete agent-filled munitions. The facts and circumstances enumerated in this document indicate that current decontamination practices are safe, scientifically valid, and result in the total destruction of agents in question.

Several basic issues were addressed:

a. Do theoretical chemical calculations support claims that agents plus decontaminants yield products that no longer contain agents? They do. Reaction energies, reaction kinetics, chemical equilibrium, laws of thermodynamics, and other mathematical considerations indicate that A + B do indeed equal C + D.

b. Are older decontamination procedures, which used different reagents, equivalent to today's protocols and reagents? In most cases, yes. For example, when using sodium hydroxide or sodium carbonate, the reactive decontaminating moiety in both cases is the hydroxyl ion (^-OH).

c. Do analytical results and toxicological data substantiate complete destruction of chemical agents when decontaminated? Yes. Extensive information accrued since 1918 provides incontrovertible scientific evidence of decontamination efficacy.

BLANK PAGE

PREFACE

The work described in this report was authorized under Project No. 1L162706A553F, Decontamination and Contamination Avoidance. This work was started in December 1987 and completed in February 1988.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public.

ACKNOWLEDGMENTS

The authors wish to thank James Manthei and his group for the toxicology testing reported in this report. We also wish to thank Timothy A. Blades and his group for their help in setting up and testing the large scale decontamination procedures reported in this report.

BLANK PAGE

Table of Contents

BLANK PAGE

SUPPORT FOR THE DELISTING OF DECONTAMINATED LIQUID CHEMICAL SURETY MATERIALS AS LISTED HAZARDOUS WASTE FROM SPECIFIC SOURCES (STATE) MD02 IN COMAR 10.51.02.16-1

1.0 INTRODUCTION

1.1 REGULATORY BACKGROUND

In January 1986 the State of Maryland enacted regulations that identified certain chemical warfare agents (also known as chemical surety materials - CSM) as hazardous wastes. Included were nine listed waste solutions identified in the regulation as the following: Industry, Military; EPA Hazardous Waste Number K991-K999. According to the State, these decontaminated residues were included to make it clear that treated wastes were of concern.

Personnel from the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) noted that decontamination procedures convert the chemical agents in question to non-surety products, and requested guidance in addressing this issue.

The State offered that if CRDEC personnel document that decontaminated residues contain no detectable levels of CSM, this information could be used as a basis to consider delisting the waste residues. Specifically, the State asked that CRDEC:

a. Provide a detailed description of actual decontamination processes including a step-by-step outline of each procedure, identification of the decontaminating agent used on each agent, the theoretical chemical reaction, the concentration of decontaminant used, amount of time each reaction is allowed to proceed, plus any parameters that influence the degree to which a reaction goes to completion.

b. Describe procedures which assure that solutions used to perform toxicological tests are equivalent to solutions which result from the actual decontamination procedures.

c. Describe the protocol for toxicological testing in order to determine whether it follows generally accepted practices.

This document has been prepared by CRDEC for review by State of Maryland and other regulatory officials to assure that current standard decontamination procedures result in wastes which can be excluded from regulations as hazardous.

1.2 INSTITUTIONAL HISTORY

The agency now known as CRDEC has been located on Gunpowder Neck peninsula in Harford County, Maryland since 1918 when the land was bought by the War Department. The impetus for this purchase was the unprecedented and devastating use of chemical warfare agents during World

War I (Allied forces suffered more than one-third of their casualties as a result of chemicals). The basic mission--defense against chemical and biological agents, and providing a chemical retaliatory capability--has remained unchanged for more than seventy years.

CRDEC is unique among military entities: it is one of the very few that has Joint Service responsibilities. In other words, it executes its mission on behalf of the Army, Navy, Air Force, and Marines. All U.S. fighting forces thus depend entirely on CRDEC to provide the decisive edge in combat on a contaminated battlefield. Major support includes: gas masks and filters for armored vehicles and buildings; protective clothing; decontamination formulations and devices; methods to avoid contamination such as self-decontaminating coatings and surfaces; detectors and alarms; and retaliatory chemical munitions should deterrence fail.

Therefore, CRDEC scientists, engineers, and technicians have dealt continuously and for more than seventy years with all aspects of chemical agents and munitions, have accrued a record of laboratory safety, and have become uncontested leaders in innovative research and development as well as proper decontamination of chemical surety materials in the Western World.

This legacy, reflected in bibliographical citations, reaches back to 1918 - e.g., "The Cleaning of Objects Contaminated with Yperite [Mustard]", Chemical Warfare Service Report No. Z-197, May 1918, Washington, D.C., and "Solubility and Rate of Hydrolysis of Mustard Gas in Water", R. E. Wilson, *et al.*, *Journal of the American Chemical Society* **1922**, *44*, 2867. The point is that CRDEC scientists and engineers are free-world experts in decontaminating chemical warfare agents.

Extensive decontamination experience and comprehensive data bases have underwritten huge demilitarization projects in the past including GB-filled M55 rockets, and M139 and E139 bomblets at Tooele Army Depot, Utah. In all cases, decontamination and disposal projects for agent-filled munitions were executed safety, without untoward incident, and in total compliance with every prevailing environmental and human safety requirements and concern. These and other facts enumerated in detail in this document provide ample evidence that current decontamination protocols and procedures are safe, scientific, and result in the total destruction of chemical agents.

1.3 BASIC ORGANIZATION OF THE DOCUMENT

To be responsive to the State's requests, this manuscript has been organized into the following general areas:

(1) The theoretical chemistry basis for asserting that agent plus decontaminant yields less-hazardous products. Included in this section are discussions of the agents listed, decontamination operational definitions (i.e., how clean is clean?), decontamination procedures, theoretical reaction

mechanisms and kinetics involved, and theoretical bases for analyzing reaction products.

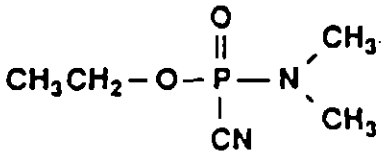
(2) The issue of equivalence in chemical-agent decon. For example, if an older, standard decontamination procedure was based on using sodium carbonate and the modern version prescribes sodium hydroxide, one might conclude that there is no scientific basis upon which to compare results. On the contrary, the active decon moiety in both cases is the hydroxyl ion (·OH), and the agent being decontaminated reacts exactly the same.

(3) Archival data. Since 1918, information has accrued about decon efficiency from sources as varied in scope and complexity as sophisticated laboratory experiments, combat operations, training exercises, field trials, and wholesale destruction of unserviceable munitions. The data used here are in two forms, analytical and toxicological, and provide a comprehensive foundation upon which to structure conclusions of efficacy.

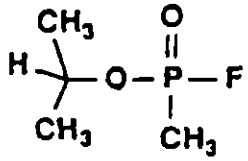
(4) Analytical methods. A review of methods utilized to determine the concentration of active material before and after the decontamination process. Included are the most recent literature from both CRDEC and other agencies involved in Decontamination methodology.

2.0 Decontamination

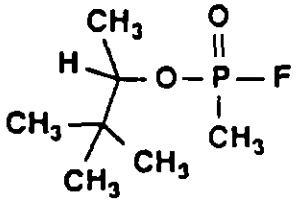
2.1 Agents (State of Maryland Listing)



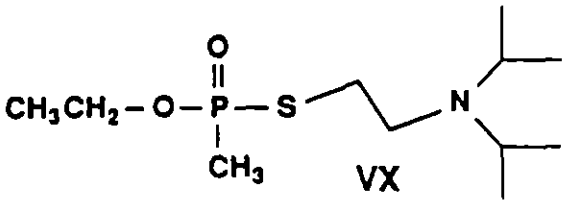
GA (Tabun)



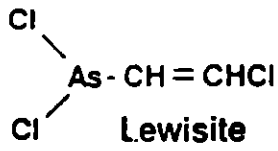
GB (Sarin)



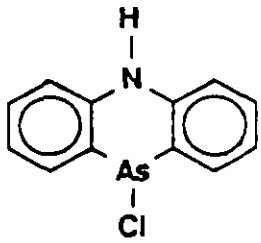
GD (Soman)



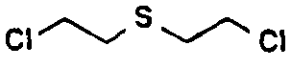
VX



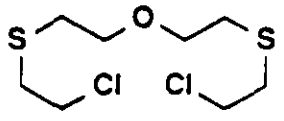
Lewisite



Adamsite



HD - (Mustard)



T

2.2 Decontamination Operational Definitions

Over the years, several reviews have been published concerning chemical warfare (CW) agent decontamination. These reviews have generally focused on fielded and/or experimental systems which have been used to detoxify agents. But, what is decontamination? The answer, like that to the question "What is clean?", is not simple or direct. In field expedient decon, the procedure may be anything which delays the toxic effects of an agent, to a level below which the problem may be ignored. The purpose of such a decon action is to reduce the need for wearing maximum individual protective gear and/or to reduce the likelihood of exposure to agent. Deliberate decon, in contrast, is administered under controlled conditions and has at its basis removal from the environment of the maximum amount of the toxic material - - in the best case not only below toxic levels but below all detectable concentrations. Its goal is to remove all contamination so that equipment may be returned to service or sent to a maintenance facility without presenting a hazard to unprotected personnel.

Decontamination by purely physical processes is thus undesirable as it does not solve the problem, but only moves it to a different location. Use of a chemically reactive system which can convert the CW agents to non-toxic materials remains the most viable approach. Once it has been decided to chemically react, and thus destroy, an agent, questions immediately arise concerning the level of chemical destruction and kinetics and products produced. In deliberate decon a minimum requirement is that 10 half-lives of destruction to less-toxic products must be obtained during 10 minutes at room temperature. Starting with this minimum requirement, the chemistry described below is aimed at increasing the speed of destruction and the control of the products to the lowest possible level to ensure no toxic exposure after decontamination. This usually means that decontamination is not considered complete unless greater that 99.9% destruction to less-toxic products is certified.

2.3 Theory of DECON Procedures

2.3.1 Introduction

Chemical equations depict reactions between molecules. They conventionally are written to show initial reactants and final products; i.e., A + B $\rightarrow$ C + D.

But this is the most elementary sort of scientific stenography, for confounding arrays of conditions and factors exist within the molecular milieu, however, simplistically transcribed.

For molecules to react, particles (e.g., agent and decontaminant) must collide, and these collisions must result in interactions between particles. The Laws of Thermodynamics decree that reactions proceed from higher to lower energy states. Factors that influence the rate of a chemical reaction include the

nature of reactants, amount of contact area, concentration of reactants, temperature and, in some cases, presence of a catalyst.

Other factors are involved in determining the degree of completeness of chemical reactions. In many instances, time is of obvious importance. Some reactions achieve an equilibrium state in which A + B and C + D are present in discrete concentrations. If, for example, compound "B" is a chemical warfare agent and a state of equilibrium has been reached whereby some "B" remains, the conversion of "B" can be driven to completion by adding an excess of reactant "A" (or, conversely, by removing some of the products "C" and "D"). This effect of concentration on chemical equilibrium was succinctly summarized by Henri Le Châtelier (1888): "Any change in one of the variables that determines the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change in the variable under consideration." In the same way, the rate of many slow decon reactions can be accelerated by adding excess concentrations of decontaminant.

Phase separations (e.g., physically resembling oil on water) can cause reaction rates to be painfully slow because agent and decon molecules react only at the interface. Effective mixing is normally employed to solve this problem.

Other factors (such as pH or side reactions) can also influence the ultimate objective of any decontamination exercise: that is, the complete destruction of a chemical agent.

In the following sections of this document, the theoretical basis for each decontamination reaction is elucidated.

The theoretical treatment comprises three basic approaches:

a. Thermodynamics (2.3.2). The reactions described should work because all are going "downhill" from higher to lower energy states.

b. Kinetics (2.3.3). Rate constants, half-lives, and other mathematical expressions are employed to calculate how fast decon reactions proceed.

c. Product analysis (2.3.4). In this "materials balance" section, predictions of chemical structures and amounts of products are calculated based on the assumption that 100 percent of the chemical agent is converted to products.

2.3.2 Thermodynamics of DECON Procedures

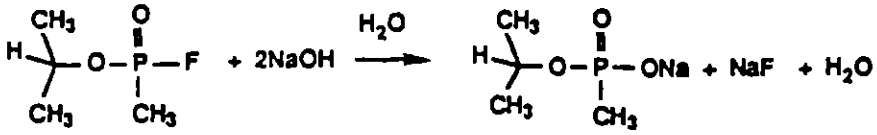
In the reaction between an agent and a decon solution, several possibilities must be considered. Using the base hydrolysis of GB as an example, three plausible events may occur to affect the net amount of GB in the Decon solution:

1. The neutralization reaction may proceed, reducing the GB concentration.

2. Sodium isopropyl methylphosphonate may be reconverted to GB (reformation of agent).

3. GB may evaporate from the reaction mixture and be vented into the environment.

We first consider possibilities 1 and 2 together. The reaction of GB with hydroxide, shown below:



is highly exothermic, with a free energy of about -30 kcal/mole. The heat generated by this reaction is such that precautions must be taken to prevent overheating of the reaction vessel in bulk decon procedures. The rate of this reaction increases with increasing temperature and pH. Since the reaction mixture and the neutralized brine contain an excess of base (NaOH or Na_2CO_3), any evaporation of water from the brine will increase the pH of the solution and hence speed the reaction. Thus the equilibrium constant of the reaction can be calculated from the free energy of the reaction:

$\Delta G = -2.303\ RT \log K_{eq}$

where R is the gas constant, ΔG the free energy, T the absolute temperature and K_{eq} the equilibrium constant. In the decon reaction the temperature is generally close to room temperature (25°C, 298 K), so:

$-30{,}000\ cal/mole = -2.303 \times 1.987\ cal/mole{\cdot}^oK \times 298\ K \times \log K_{eq}$,

or $\log K_{eq} = 21.9$. Thus in theory the conversion of GB to sodium isopropyl methylphosphonate should be nearly complete.

Epstein, *et al.* (1977) discussed the possibility of reconversion of sodium isopropyl methylphosphonate to GB in the presence of HF or other acids in the vapor above the salt solution. Two requirements for this reaction are an acidic environment and an absence of water to shift the equilibrium of the reaction to formation of GB (neither condition exists in the normal liquid decon procedures). However, even if this reaction does in fact occur, the "new" GB would have two fates: reaction in the basic salt solution, or venting into the atmosphere. The first possibility is the initial reaction discussed above and reformation in solution would again subject GB to reaction with NaOH.

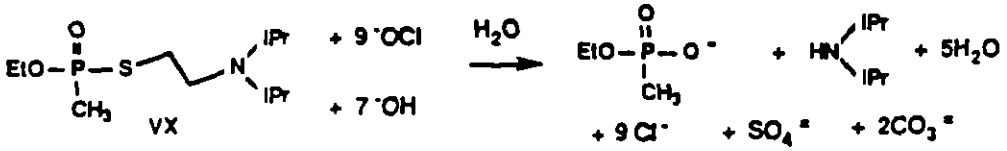
Considering the second possibility, the temperature of the decon solution is 25°C, much lower than the boiling point of GB (148°C). From the heat of vaporization of GB, we may calculate the change in its vapor pressure as a function of temperature by applying the Clausius-Clapeyron equation:

$$p = p_0 e^{(-\Delta Hvap/RT)}$$

where p is the vapor pressure, p_0 is a constant, and ΔHvap is the heat of vaporization, presumed constant over temperature. Using ΔHvap = 11.9 kcal/mole the vapor pressure of GB is 2.2 mmHg at 25°C (298 K).

At room temperature, considering the vapor pressure and the equilibrium constant calculated above, it is unlikely that vaporization would occur. Neither reformation of "new" GB nor vapor buildup appear to pose a hazard. GB was used in this example because of the listed agents it is the most volatile and would be the most likely to vaporize from the reaction media, if that were of concern.

Another example of thermodynamics is illustrative. The recommended procedure for decontamination of VX is reaction with alkaline hypochlorite (usually HTH, calcium hypochlorite). Compounds isolated and/or identified from reactions of VX and bleach solutions are calcium sulfate, diisopropylamine, and ethylmethylphosphonic acid. Based on these observations, the equation for the reaction of VX with alkaline hypochlorite solutions is:



With HTH, the anions precipitate as the calcium salts.

The heats of reaction, according to the equation above, can be calculated from bond energies, heats of formation and heats of neutralization to be 685 kcal/mole (Epstein, 1973). Laboratory determination (small scale - very dilute solutions) of this reaction gave 471 ± 3 kcal/mole. Larger scale reactions (similar to actual bulk decon procedures) gave a value of 675 ± 13 kcal/mole, a figure close to the theoretical value from bond energies. If any of the three values, one from calculation and the other two from experimental data, are substituted into the equation used to calculate the equilibrium constant (see GB discussion above) the conclusion is that tremendous energy is released in this oxidative destruction of VX and the equilibrium lies dramatically toward products under the conditions of the decon reaction.

Thus the calculations above suggest that the equilibrium constants for the reaction of GB with caustic (hydrolysis) and VX with hypochlorite (oxidation)

should favor the hydrolysis product by a very large margin and that reformation of "new" agent from the reaction products is negligible under standard decon conditions. Similar energetics exist for all the listed agents.

2.3.3 Kinetics of DECON Procedures

The fact that the driving force for a reaction is large (ΔG is a large negative quantity) does not mean that the reaction will necessarily occur under any given conditions. An example related to combustion is the mixture of hydrogen and oxygen at room temperature. For the reaction,

$$H_2 + 1/2O_2 \rightarrow H_2O$$

the free energy is -54.64 kcal/mole. Despite the large negative free energy term, the reaction mixture may be kept safely for decades without detectable reaction. However, a pinch of platinum-sponge (catalyst) causes the mixture to react violently (i.e., explode). The necessary affinity for reaction certainly exists in this system (thermodynamics), but the rate of attainment of equilibrium (chemical kinetics) depends on different factors.

Numerous other examples of this situation exist. Magnesium and aluminum oxidize with a very large free energy change (in excess of 100 kcal/mole). At room temperature the small film of oxide which forms on these metals makes further reaction extremely slow (thus allowing the use of these metals in structural environments). The equilibrium condition is never reached in our lifetime - - the usual time frame of importance. Incendiary bombs and the thermite reaction, on the other hand, are reminders that a large free energy in this reaction is a valid measure of the enormous affinity of the reactants to transform themselves to products.

Knowledge of the rapidity at which a reaction attains equilibrium is thus separated from the energetics of the overall reaction.

Decomposition of agent (again, for example GA) in aqueous or largely aqueous media should follow a rate law of the form:

$$\text{rate} = k_{hyd}[GA] + k_{OH}[OH^-][GA] + k_{CAT}[CAT][GA]$$

$$= \{k_{hyd} + k_{OH}[OH^-] + k_{CAT}[CAT]\}\,[GA] \qquad (1)$$

where the $k_{hyd}[GA]$ represents the hydroxide-independent "background" reaction, the $k_{OH}[OH^-][GA]$ represents the second order reaction between ^-OH and GA, and the $k_{CAT}[CAT][GA]$ term is the rate enhancement resulting from the addition of catalyst to the system.

Hydrolysis reactions are usually run where both water and hydroxide are in large excess. Under these conditions the first two terms of equation (1) ($k_{hyd} + k_{OH}[OH]$) are constant. If when catalyst is also in large excess over substrate ([CAT]>>[GA]) (or if catalyst is not consumed in the reaction), then the third term

is also essentially constant. Under these conditions equation (1) reduces to a description of an experimentally first-order process:

$$\text{rate} = k_{obs}[GA] \qquad (2)$$

where

$$k_{obs} = k_{hyd} + k_{OH}[OH^-] + k_{CAT}[CAT] \qquad (3)$$

Since in this example the system is restricted to hydroxide (no catalyst added), the term $k_{CAT}[CAT]$ reduces to 0 and the overall observed rate may be expressed as:

$$k_{obs} = k_{hyd} + k_{OH}[^-OH] \qquad (4)$$

Equation (4) forms the basis of the kinetic analysis. Experimental data are plotted as k_{obs} vs. [OH]. Experimental plots of agent hydrolysis are consistent with the linear relation predicted by equation (4). A linear least-squares routine is used to determine the statistically most valid slope (k_{OH}) and intercept (k_{hyd}, no added hydroxide) for each experiment to determine the best data set. Computer analysis on each data set is then performed to compare the experimental data with a theoretical analysis based on assumption of a first order kinetic process. If the experimental values lie on the curve predicted by the assumed first order fit, then this is strong indication that the process is indeed acting as a first order kinetic process. Such experimental data are usually collected for five or more half-lives (*i.e.*, >96% reaction) to ensure good statistical analysis.

What is the value of this type of analysis? First, in the description of a kinetically first order process, the half-life of reaction ($t_{1/2}$) is independent of the concentration of agent, and is expressed as follows:

$$t_{1/2} = (\ln 2)/k_{obs}$$

Thus a measured half-life at high agent concentrations (experimentally easy to measure) is valid for agent destruction when the concentration of agent is low (experimentally difficult to measure). In a first-order reaction, it takes just as long to reduce the reactant concentration from 0.1 mole per liter to 0.05 mole per liter as to reduce it from 10 moles per liter to 5 moles per liter.

A graphic example of the predictive power of the first order kinetic condition is shown in the following table. We assume, in this example, an "agent" whose molecular weight is 100, and where we start to decon a solution of 100 g agent/L in excess aqueous hydroxide:

Initial Quantity (g)	Half-Lives	Quantity Remaining (g)	% Destroyed
100	0	100	0
100	1	50	50
50	2	25	75
25	3	12.5	87.5
12.5	4	6.25	93.75
6.25	5	3.125	96.875
3.125	6	1.5625	98.4375
1.5625	7	0.78125	99.21875
0.78125	8	0.390625	99.609375
0.390625	9	0.1953125	99.804687
0.1953125	10	0.0976562	99.902343
0.0976562	11	0.0488281	99.951171
0.0488281	12	0.0244140	99.975585
0.0244140	13	0.012207	99.987792
0.0122070	14	0.0061035	99.993895
0.0061035	15	0.0030517	99.996946
0.0030517	16	0.0015258	99.998471
0.0015258	17	0.0007629	99.999233
0.0007629	18	0.0003814	99.999614
0.0003814	19	0.0001907	99.999804
0.0001907	20	0.0000953	99.999899

[Remaining agent, column three, may be calculated from the formula $100/2^n$ which is the fraction of agent remaining, when starting with 100g, after n half lives. In general, the agent remaining when subjected to a first-order kinetic rate pattern is initial quantity/2^n, the fraction remaining after n half-lives.]

It can be seen that even when starting from a very concentrated solution the reduction in material is significant by 10 half-lives (99.9% destruction) and even more so at 20 half-lives (99.9999%).

Another value of this kinetic treatment is the determination of the "second order rate constant", k_{OH}, for the reaction. If we assume that the background hydrolysis rate is small (experimentally verified), then the major contribution to the overall rate is the hydroxide-dependent part of the reaction. This "second order rate constant" allows the calculation of the observed first order rate if the concentration of hydroxide is known. For example, if the second order rate constant between GA and hydroxide is 7.5 $M^{-1} \cdot s^{-1}$, and the concentration of hydroxide is 0.01 M (equivalent to a pH of 12), then the following calculation may be performed:

$k_{obs} = k_{OH}[OH^-]$

$k_{obs} = [7.5\ M^{-1} \cdot s^{-1}][0.01\ M] = 0.075/s$

Once the observed rate constant is calculated, then the half-life of the reaction may be calculated using the relationship:

$t_{1/2} = (\ln 2)/k_{obs}$

$t_{1/2} = (0.69)/0.075/s = 9.2$ seconds

This calculation thus allows us to state that in 92 seconds (1.53 minutes, 10 half-lives) in 0.01 M hydroxide we will have destroyed 99.9% of the initial GA present in the decon solution. In 184 seconds (3.06 minutes, 20 half-lives) in 0.01 M hydroxide 99.9999 % of the initial GA will be reacted.

Once the "second order rate constant, [k_{OH}]" is known, the half-life at any specified hydroxide concentration may be calculated. Thus if the pH is raised from 12 to 13, the hydroxide concentration should be raised from 0.01 M to 0.1 M. From the equations above it can be predicted that the destruction of GA would proceed with a half-life of about 1 second, and that after 1 minute the concentration of GA would be below the ppt level.

Representative "Second Order Rate Constants" for Hydrolysis of Nerve Agents

Substrate	k_{OH} ($M^{-1} \cdot s^{-1}$)	$t_{1/2}$ (sec) at pH = 12
GA	7.5	9.2
GB	25	3
GD	10	7
VX	0.083	835

(Note: In the kinetic analysis there are three terms, the last being a catalytic term. In the usual decon solutions only hydroxide is used; however, there are catalysts which are known to accelerate the hydrolysis rate over the one observed related to base concentration. In field expedient decon this allows the reaction to proceed rapidly at lower pH's. This is of great practical interest when deconning sensitive materials. The kinetic analysis is developed to analyze the effect of added catalyst, if present in the decon system.)

2.3.4 Products of DECON Procedures

There are a number of commonly used methods for determining material balance criteria in decontamination reactions. In most cases one method is not sufficient, and the problem is generally approached from several directions. Obviously any mechanism proposed for a transformation must account for all products obtained and for their relative proportions, including products formed by side reactions. A proposed transformation cannot be correct if it fails to predict the products in approximately their correct proportions.

Traditionally the most satisfying method used to handle the mass balance problem has been to isolate the products involved. This technique is powerful but fraught with difficulties: first, large concentrations of materials must generally be utilized to ensure good isolation; second, there is always the concern that the major products of the reaction will be identified but minor products will be missed. For example, assume a hypothetical decon reaction produces two acids, acid A in 90% and acid B in 10% yield. Crystallization is a common method used to isolating acids. In the crystallization process, molecules gradually deposit from solution and attach to each other in an orderly array known as a lattice. As the aggregates of molecules grow large enough to be visible, they appear as crystalline materials. The high symmetry of these macroscopic aggregates suggests the ordered arrangement of the crystal lattice. Molecules which do not have precisely the same kinds and arrangement of forces cannot be held in the lattice. Smaller or larger molecules of similar structure are thus excluded; i.e., in the isolation of acid A, acid B will probably be excluded by the forces active in the crystallization process. Acid B will therefore be missed in the overall study. All direct isolation methodology suffers from this consideration.

In many reactions, intermediates between starting material and products are proposed. Identification of a possible intermediate is critical since an intermediate, although present in small quantities, may have toxic attributes, the final product lacks. Numerous ways, none foolproof, are used to learn whether or not a proposed intermediate is present and, if so, its structure. This problem can be subdivided into several areas. The intermediate can be isolated if it is sufficiently stable. If this isolated intermediate can be shown to proceed to products when subjected to the reaction conditions, strong evidence thereby exists that the reaction proceeds through such an intermediate. If isolation of the intermediate is unsuccessful, some spectral technique such as infrared (ir), nuclear magnetic resonance (nmr), etc., may be used. These are extremely powerful procedures which give a direct measure of the quantity and structure of an intermediate. A third variation traps the intermediate by an externally added trapping agent. In the last variation the proposed intermediate is independently synthesized then subjected to the reaction conditions thus demonstrating the products are formed. All of the techniques for determination of an intermediate lends credence to the suggested transformations of starting material to products.

Several other methods, used in conjunction with one another, provide information on product distribution. For example, isotope labeling of starting materials allows the path of reaction-to-products to be traced even under very dilute conditions. Historically use of the radioactive isotope carbon-14 has shown the power of this technique, but recent advances in analytical methods allow the use of stable (non-radioactive) isotopes in this regard.

Kinetic evidence is an extremely powerful technique in the identification of mechanism and material balance. The question being asked is: "Does the rate of disappearance of starting material equal the rate of appearance of an

identifiable product?" If this correlation can be clearly shown it is a powerful indicator of the material balance of the reaction.

As stated in the introduction, no one technique is clearly useful in all cases, but a combination of techniques draws on the power of each method. One difficulty when examining the literature of decontamination reactions is that many products of the decon reaction are difficult to analyze by traditional analytical techniques. As a result much archival information is based on the kinetic argument involving disappearance of reagents and a hypothesis of products, based on the kinetic evidence available. It has only been in the last decade that analytical techniques have been developed which allow the chemist to directly observe the products of these reactions. Use of these techniques has consistently confirmed earlier hypotheses based on kinetic analysis.

Several examples are illustrative in this regard. In the early 1980's it was discovered at CRDEC that enzymatic catalysts existed for the destruction of toxic nerve agents. Analytically the reaction was monitored by the appearance of fluoride using a fluoride ion electrode. The hypothesis of hydrolysis indicated that for every GB molecule hydrolyzed only fluoride was released. When the rate of disappearance of GB was correlated with the appearance of fluoride the rates were mirror images of one another. Although the isopropyl methylphosphonic acid was not directly analyzed, a strong implication existed that it was the only reasonable product, other than fluoride, in this decon reaction. Why then was there no direct analysis for isopropyl methylphosphonic acid to prove it is a product of the reaction? The answer lies in the analytical techniques available. Enzymatic reactions are generally run in dilute aqueous solution, and the analytical tools for directly observing isopropyl methylphosphonic acid are not as sensitive as those which detect fluoride ion. Essential in our mass balance criteria is the equation of a known amount of GB introduced into the reaction. Its disappearance is followed thus demonstrating that a known amount of fluoride is produced from the reaction mixture by equivalent rates.

Mustard hydrolysis is another case in point. Mustard dissolves in water to produced HCl. Traditionally accurate methods have been available to measure acid concentration (and, subsequently, chloride concentration). The disappearance of mustard is thus correlated with the appearance of HCl. It is encouraging that indirect kinetic studies have so often proven accurate. The classical paper on mustard reactivity of Bartlett and Swain (1946), based the mechanism on kinetic arguments and a small quantity of product isolation. It was not until the advent of nmr technology in the 1980's that direct identification of the information published in 1946 could be made. In most cases the advent of modern analytical tools has supported the suggestion in the archival literature.

We should briefly touch again on the difficulty encountered when seeking accurate data on the products of decon reactions. Many experimental techniques for accurate analysis, e.g., gc-ms, require that an aqueous reaction

media be introduced into the gas phase, then flashed, under high vacuum, into the analysis unit. The conditions of this analysis are grossly different from the conditions which existed in the aqueous decon solution. Thus, there is always concern that the analysis is not truly indicative of the situation in solution.

One extraordinary powerful technique which has recently become available to the chemist is nuclear magnetic resonance (nmr) spectroscopy. A recent development, even by chemical standards, the first nmr signals were observed in 1945 by Felix Bloch at Stanford (octane) and Edward Purcell at Harvard (water). The three-line spectrum of ethanol was reported in 1951, and in 1953 Bloch and Purcell shared the Nobel prize for their discovery. By that year, Varian Associates had delivered three nmr machines to Exxon, DuPont and Shell.

It is known that a moving electric charge creates a magnetic field. Atomic nuclei, which are known to have a charge, should also create a magnetic field if they spin. Many isotopes have what appears to be a mechanical spin, to which a spin angular momentum is assigned. All microphysical systems are quantized, and it is the spin number, i.e., the maximum observable angular momentum for the nucleus, which concerns us. For purposes of this discussion, it will suffice to say that certain nuclei exhibit this property. For example, ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P all have spins of 1/2. Frequently encountered nuclei which have no spin are ^{12}C, ^{16}O, and ^{32}S.

Every isotope with a spin not equal to zero will be characterized by a nuclear magnetic moment, which is represented by a symbol μ. This can be thought of as a bar magnet with a strength μ. If the nucleus (bar magnetic) is placed in a magnetic field, there will obviously be an interaction. Like a bar magnet, the nucleus must be either attracted to or repelled by the magnetic field. Since only two possibilities exist for a system with a spin of 1/2, there are only two possible orientations in the magnetic field, referred to as plus and minus. Thus it is clear that the nmr method requires a magnetic field as well as an external energy source. The result of some simple mathematics (not discussed here) reveals that an energy transition from a minus to a plus state may be measured. It is relatively easy to conceptualize what happens in the nmr experiment. In the absence of a magnetic field, the nuclear spins are randomized in all possible directions. When a magnetic field is applied, the spins tend to be oriented either in the same direction as the applied magnetic field (low energy state) or opposite to it (high energy state). As the molecule encounters incident radiation, energy absorption occurs and one of the spins flips direction. This energy absorption is what the nmr system detects.

The discussion of nmr theory given above only requires that the nucleus of an atom have a magnetic moment for observation of the nmr phenomenon. Large numbers of nuclei contain a magnetic moment and are thus candidates for the nmr experiment. Nuclei commonly dealt with by organic chemists which give an nmr signal under appropriate conditions include ^{13}C, ^{31}P, ^{19}F, ^{15}N, and even such ions as ^{23}Na.

The insensitivity of early instruments presented problems for nmr spectroscopy. Although many elements can be considered in the nmr technique, only nuclei which give strong signals (hydrogen, fluorine) and/or are present in the sample in high molecular concentration are practical to measure. The stable natural carbon isotope ^{13}C is present in 1.1% abundance (^{12}C has no magnetic moment). A very sensitive measuring technique is needed to determine the signal from these atoms. Recent instrument advances of the last decade have produced great sensitivity which allows routine measurement of ^{13}C spectra on normal samples. The same is true for ^{31}P spectra. In addition, both types of spectra cover a large range in the energy spectrum (i.e., ^{13}C signals range from 0 - 250 parts per million).

This technique, **because it directly observes the nuclei of an individual molecule can provide not only information of the disappearance of starting material but the appearance of product in the same experiment.** Most toxic agents contain phosphorous (^{31}P) which as indicated above gives an nmr signal. From the signal position of the phosphorous atom the group which surrounds it can be determined. In the hydrolysis of GB, the ^{31}P signal can be measured in the starting material, then watched for the shift in the ^{31}P signal to a new position as the decon reaction proceeds. It is extremely unlikely that two completely different compounds will produce the same signal in this technique. Thus, a direct non-destructive probe into the decontamination reaction is possible by watching the shift in various atoms in the starting material and products. In general, these measurements confirm literature suggestions in the archival literature. However, this is a direct observation of products under the decon solution and a certification that the toxic starting materials do not exist in solution, within the limits of sensitivity of the technique. [Note: usually anything in excess of 0.5% will be detected using this technique. Therefore a more accurate statement would be that the concentration of starting material has decreased to a level less that 0.5% of its initial value, or that the starting material is 99.5% destroyed. Specialized techniques, not discussed here, allow the nmr technique to measure down to limits of 0.01% under special circumstances.]

The time frame of the nmr experiment also permits a crude confirmation of the kinetic data discussed in 3.3.3. In other words when GB is subjected to Na_2CO_3 hydrolysis under the approved SOP, ^{31}P measurements in the nmr confirm that the only product observed is isopropyl methylphosphonic acid, and that this product is identical to the product of sodium hydroxide hydrolysis. This nmr experiment measures the chemical equivalence of these two decon procedures and ensures that this reaction goes to the indicated products to greater than 99.5%.

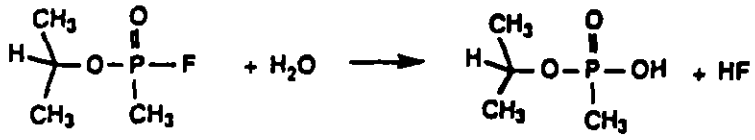
The above discussion indicates that in all the reactions under consideration the following information is available. (1) There exists an enormous thermodynamic drive to convert these toxic materials into non-toxic products. (2) Not only is there a large energetic drive to these reactions, but there is also a rapid kinetic mechanism for these transformations. (3) The product analysis discussed above demonstrates that the starting materials have

been indeed destroyed and the products clearly identified as those suggested in the archival records.

3 Equivalence of DECON Procedures

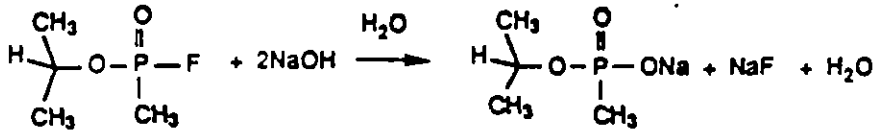
A review of the archival literature available from 1917 to the present day clearly indicates the two major chemical procedures effective in the destruction of toxic chemical agents are hydrolysis and oxidation. Within these two broad categories, however there appear numerous reagents suggested in various decon procedures. Although, at first glance, these procedures appear to be different, on close examination there are fundamental similarities in the active chemical principles responsible for decontamination. In other words, although the suggested procedures require different decontaminating agents (usually chosen for compatibility with various materials to be cleaned), the reactive species responsible for the decontamination are the same. An excellent example of this chemical equivalence is found in the base-catalyzed hydrolysis of the nerve agent GD.

In general, the term hydrolysis is utilized to indicate the addition of water to a reactive molecule with the elimination of some fragment, after the addition of water, into the aqueous solution. In the example under discussion, water will react with GB to produce one mole of hydrogen fluoride and one mole of GB acid according to the following reaction:



Therefore, mere dissolution of GB in water is in itself a decontamination procedure (sometime termed "weathering" when dealing with field decontamination). Because hydrolysis of GB in distilled water is slow, it is not considered a good decon procedure per se.

However, if sodium hydroxide (NaOH) is added to a water/GB solution, a rapid bimolecular reaction is observed whereby hydroxide attacks the phosphorous center and subsequently releases a fluoride ion. Hydroxide is well known in the chemical literature not only as a strong base but as a excellent nucleophile. Thus the hydroxide anion attacks the phosphorous to form a transient intermediate, which then decomposes to produce fluoride anion. In the study of this reaction it is observed that increasing the hydroxide concentration increases the reaction rate; i.e., it is a bimolecular reaction which is dependent on the concentration of hydroxide. In practical terms, although only one hydroxide is involved in the initial attack at phosphorous, two molecules of hydroxide are consumed for every molecule of GB hydrolyzed because one of the products is itself an acid, isopropyl methylphosphonate. This second acid-base reaction is itself advantageous as it prevents the isopropyl methylphosphonate from re-reacting with fluoride to form GB. Thus the overall stoichiometry of sodium hydroxide with GB is represented by the following:



Note that the reaction produces one mole of fluoride ion, one mole of isopropyl methylphosphonate (GB acid anion), and consumes two moles of hydroxide.

The stoichiometry above demonstrates why NaOH is recommended as a decon reagent. NaOH is very soluble in both aqueous and aqueous alcoholic solutions, and is a potent nucleophile and base in almost all solutions. It is one of the first decon reagents to be used in the chemical-warfare arena and continues to enjoy popularity as a rapid, complete and inexpensive procedure. Note in the NMR data in the attached appendix that the sole product of the hydrolysis of GB in aqueous sodium hydroxide is clearly isopropyl methylphosphonate reaction (GB acid). Note also that the reaction is complete (>99.5%) in less than 10 minutes.

Why, if hydroxide is such an effective decon reagent, are numerous other solutions recommended to perform this transformation? The answer is that this NaOH is very corrosive. This solution is extremely damaging to many metal surfaces and is potentially quite damaging to skin, clothes, and other materials. Of particular concern is the well-known reaction between aqueous NaOH and aluminum metal. This reaction produces hydrogen gas in a very exothermic transformation and is extremely damaging to any component which contains aluminum. In several industrial processes this reaction between hydroxide and aluminum to form sodium aluminate (producing heat) is used commercially, and is often found in household drain cleaners such as "Drano." Therefore, the decontamination of equipment which contains reactive metals such as aluminum or magnesium requires alternative reagents to hydroxide in order to suppress this corrosive reaction. One of the most useful is the substitution of sodium carbonate for aqueous sodium hydroxide in the decontamination solution. At first glance this seems a major change in the decon procedure, but, in fact, sodium carbonate is well known to react with water to produce sodium bicarbonate and hydroxide according to the following reaction:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH$$

The advantage to this procedure is that it produces an alkaline aqueous solution (a solution defined as containing a greater concentration of OH^- ions than H^+ ions) when dissolved in water, and undergoes hydrolysis to yield sodium hydroxide which then may proceed to act as a potent reagent against GB. The major advantage to sodium carbonate is that although it releases hydroxide in the solution on a steady basis, the hydroxide is simultaneously consumed by another reaction (i.e., the reaction with GB to form isopropyl methylphosphonate and floride, reaction given above). ***Thus sodium***

carbonate, although not as powerful a reagent as pure sodium hydroxide, produces sodium hydroxide in solution and is chemically equivalent to hydroxide in its chemistry.

In the following table note the pH relationships between sodium hydroxide, sodium carbonate, and other similar bases. Note also that a 0.01 M solution of sodium carbonate has approximately the same pH as 0.001 M sodium hydroxide. When used as a decon solution, therefore, sodium carbonate is a mild source of hydroxide ion (the active nucleophile in solution) and thus is more advantageous as a decon reagent when aluminum and other reactive metals are exposed to the decon process.

Approximate pH Values for Various Concentrations of Selected Bases

Compound	1N	0.1N	0.01N	0.001N
Ammonia	11.8	11.3	10.8	10.3
Potassium Hydroxide	14.0	13.0	12.0	11.0
Sodium Carbonate	-	11.5	11.0	-
Sodium Hydroxide	14.05	13.07	12.12	11.13

In the attached appendix it can be seen that both GB and GD are hydrolyzed in aqueous sodium carbonate, aqueous sodium hydroxide, and alcoholic sodium hydroxide to form rapidly the same decontamination products. Kinetics on these systems suggest that both GB and GD have a half-life during hydrolysis under these conditions on the order of 5-10 seconds; only one to two minutes of reaction are needed to proceed through 10 half-lives of hydrolysis. Nuclear magnetic resonance (nmr) data show that after 5 minutes essentially no GB can be observed when this technique is used. Under these experimental conditions, were GB present in concentrations greater than 0.5%, it would be clearly observed in the phosphorous spectrum. Thus product analysis (nmr data attached) and kinetic data are consistent with the observation that both NaOH and Na_2CO_3 in aqueous solutions rapidly react with GB to form isopropyl methylphosphonate anion and nothing else. The usual recipe for using sodium carbonate recommends the solution remain in contact with agent for 30 minutes. If, at 5 minutes, 10 half-lives of reaction are completed, then in 30 minutes approximately 60 half-lives of reaction will have been completed. This allows a calculated theoretical concentration of GB in aqueous sodium carbonate at well below the ppt level (see discussion of kinetics below).

In many other decon solutions, hydroxide or a hydroxide-producing reagent is recommended. Note the use of amines in various decontamination formulations. Again, amines dissolved in water are well known to hydrolyze to form aqueous hydroxide by the following reaction:

$$R_3N + H_2O \rightarrow R_3NH^+ + HO^-$$

This reaction is most often encountered in the use of commercial cleaners which contain ammonia. Ammonia, an amine very soluble in water, dissolves to form ammonium hydroxide, NH_4OH. It can therefore be seen that aqueous ammonia solutions are a source of hydroxide ions as is sodium carbonate. Substituted amines, such as monoethanolamine, dissolve in water to form hydroxide ion even more efficiently than ammonia. Therefore, any decon solution which contains low molecular weight amines rapidly produces an aqueous alkaline solution (i.e., hydroxide in solution). All evidence to date indicates that hydroxide in contact with GA, GB or GD produces a very rapid reaction to form the acid salts of these agents.

A similar situation exists with the use of oxidizing reagents. The familiar household bleach "Clorox" is an aqueous solution of sodium hypochlorite, NaOCl. This material is a chlorine oxidant of very powerful reactivity. It is an excellent disinfectant and a useful oxidizing agent against a large number of organic compounds, especially those which contain sulfur. In household cleaning applications this aqueous solution of hypochlorite oxidixes such biological materials as bacteria and fungis into non-living states. It is also useful for oxidatively degrading stains of various types to smaller, more soluble fragments which then can be removed by detergents in the washing medium.

The use of hypochlorite in decontamination against mustard (HD) and VX is similarly related to the oxidation potential of the hypochlorite anion (^-OCl). The oxidation potential of this anion is such that that care must be taken in its use because of the heat generated as reactions proceed. In most applications, aqueous solutions are recommended to moderate the oxidation reaction and reduce the danger involved. Therefore any source of hypochlorite is a good decontaminant for oxidizable groups such as mustard and VX. Numerous recipes exist for the inclusion of reagents which produce hypochlorite ion in water. These include, for example, sodium hyplochlorite (5% "Clorox" strength), calcium hypochlorite (HTH or STB) as an aqueous solution or slurry, and the soft halogens such as fichlor and chloramine B, which produce hypochlorite upon reaction with water. Thus the formulation of an oxidative decontamination solution follows the same general orthodoxy as one observes with aqueous sodium hydroxide; i.e., the choice of the oxidant depends on the substrate to be deconned, but in all cases the reagent produces a controlled amount of hypochlorite which actually performs the decon reaction. In this context sodium hypochlorite, calcium hypochlorite, or the organic N-chloramine compounds can be considered as chemically equivalent because they react with water to release hypochlorite as the active ingredient.

Yet another reactive attribute of hypochlorite is exploited in many detoxification reactions. Hypochlorite falls into the category of alpha nucleophiles (see Section 4.1.4.2), powerful reagents similar to hydroxide in nucleophilic behavior (in contrast to oxidative behavior). Therefore the hypochlorite anion will react as a catalyst with G-agents to hydrolyze the material. The underlying reason why these types of anions are such powerful nucleophiles is still debated in the chemical fraternity; however, it has been demonstrated that they are very reactive against phosphorous compounds such as GB. An aqueous hypochlorite solution is a powerful decontaminant against G-agents through this hydrolytic mechanism as it is with mustard and VX through oxidation. This dual reactivity of hypochlorite has recently exploited by the German Army's fielding of the "C8 emulsion". This recipe is an aqueous organic emulsion which contains calcium hypochlorite as an active oxidant. It is extremely powerful in decontaminating mustard and other sulfur-containing compounds. CRDEC has demonstrated that this formula is also a powerful decontaminant against G-agents. In the product analysis of G-agents, the normal hydrolytic products are rapidly produced (i.e., isopropyl methylphosphonate from GB), as shown in the nmr data (Appendix attached).

The discussion demonstrates that although numerous decontamination recipes have been suggested for various procedures, all the reagents are very similar, if not identical, in their reactive behavior and can be considered chemically equivalent decontamination procedures on a mole per mole basis. Thus, for example, no major differences should be inferred when sodium carbonate is substituted for sodium hydroxide insofar as mechanism and products are concerned. Although this view has been assumed in many early studies, it is clearly documented at present through the use of nmr technology (Appendix attached).

BLANK PAGE

4 Historical Background

4.1 Decontamination Methods - Archives

4.1.1 INTRODUCTION

4.1.1.1 Purpose and Scope of Survey

The purpose of this survey was to identify all archival material reported for the decontamination and/or destruction of the listed CW agents.

The methods used for neutralizing an agent are strongly influenced by the amount of agent present and its environment. As there is no universal decontaminant for each agent, it is desirable to have at hand a listing of all of the reported techniques, which will serve not only for ordinary situations, but also as a starting point for developing procedures for extraordinary situations.

This literature survey covers the period 1918-1987. In it are included open literature publications, government reports and industrial contract reports.

4.1.1.2 Organization of the Archival Material

Whereas a large number of decontaminating systems or methods have been studied for the destruction of distilled mustard (HD), G-Agents (GA, GB, and GD), S-(2-diisopropylaminethyl)-O-ethyl methylphosphonothioate (VX), and Lewisite (L) they can conveniently be subdivided into several categories: 4.1.2. water; 4.1.3. strong bases; 4.1.4. complexing agents and nucleophiles (other than 2.); 4.1.5 oxidants; 4.1.6. photochemical methods, and 4.1.7. physical collection. In this review, each category will be considered in turn. Where reported, the following, if available, will be included for each reference: quantity of agent processed, percent destroyed, reaction kinetics and method of analysis.

Those analytical methods that have been included in standard operating procedures (SOP) will be considered in appreciable detail in Sections 4.1.8 and 4.2.5.

4.1.2 WATER

Both fresh water and sea water, although plentiful and inexpensive, are relatively ineffective agents for the destruction of CW agents; nevertheless they have been used to wash contaminated surfaces. (1) The solubility of HD in water is low[2], 1 g/L, and the hydrolysis rate constant is relatively low (0.13 min^{-1}) at ambient temperature. (2) Mustard is 99.3% hydrolyzed at 50°C in 100 minutes.[3] Increasing the temperature of the water,[4] or using steam,[5] causes volatilization of a portion of the HD.[6] Addition of detergents, such as the alkyl

sulfonates or quaternary ammonium compounds, increases the solubility of HD 8 to 20 times, but results in hydrolysis rates 3 to 20 times slower.[2] The same situation results with the use of detergent micelles.[7]

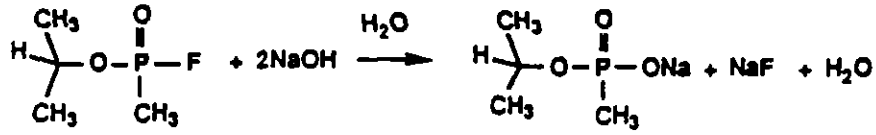
The organophosphate GB is completely miscible with water and its hydrolysis half-life in dilute solution is 75 hr at pH 7 and 25°C,[8] which is too slow from a practical standpoint for decontamination. Similarly, for VX, the values are, 30 gm/l of water (solubility), and 40 days at pH 7, respectively.[8]

Neat Lewisite (L) in water reacts rapidly to give lumps that are soluble only on prolonged stirring and are polymeric modifications of the oxide ClCH=CHAsO.[133] The aqueous solution of the oxide has vesicant properties.[134]

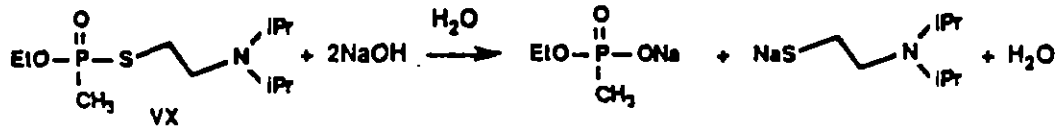
4.1.3 STRONG BASES

4.1.3.1 Aqueous Solution

Strong bases in aqueous solution may be defined as those giving a pH of approximately 11 or greater. Cleavage rates for GA, GB, GD and VX are proportional to the hydroxyl concentration (see discussion in 3.3.3), while for HD, rates in basic solution are comparable to those in water alone.[7,10,11] Unfortunately, the higher pH solutions are more corrosive to skin and to various materials. Hydrolysis of GB in strongly basic solution involves the equation:



The second order reaction rate is 30 $M^{-1} \cdot s^{-1}$ and the heat of reaction is -44.4 kcal/mole.[12] With 5% aqueous sodium hydroxide (pH > 14), the half life of GB is <0.8 sec. With respect to VX, the pertinent equation is:



The half life of VX at pH 14 is 1.3 min[13],and the second order rate constant is $30 M^{-1} \cdot hr^{-1}$, but because of its relatively low solubility in water (above about 9°C), the reaction requires a considerably longer time unless an organic solvent such as 2-methoxyethanol is included. Therefore for VX (and HD),

actual rates will be slower, depending upon the rate of solution of agent, which will depend in turn upon the degree of mixing of the heterogeneous systems.

Lewisite reacts with aqueous sodium hydroxide as follows: [134,135]

$$ClCH{=}CHAsCl_2 + 6\ NaOH \rightarrow Na_3AsO_3 + 3\ NaCl + H_2C_2 + 3\ H_2O$$

The isomeric (cis and trans) Lewisites react at different rates in 16 % aqueous sodium hydroxide, with one isomer giving almost complete acetylene evolution in 2 min and the other requiring approximately 1 hr.[136] Because of the relative insolubility of Lewisite or its oxide in aqueous solution,use of a cosolvent such as alcohol is recommended.

Many bases have been studied for decontamination. Whereas the use of 10% aqueous sodium hydroxide has been reported to be effective against HD,[14] later reports indicated the opposite.[15,16] In another report, Reichert[17] found that 125-gallon batches of HD could be effectively decontaminated with 125 gallons of water at 70°C, plus calcium oxide in excess, which raised the temperature to 100°C. The mixture was allowed to stand overnight. Analysis *via* thin layer chromatography (TLC) and gas-liquid chromatography (GLC)-mass spectrometry (MS) indicated complete hydrolysis to thiodiglycol and calcium chloride, plus some polysulfide residue that separated. The author also mentioned the use of aqueous sodium hydroxide and of ammonium hydroxide for hydrolysis of HD, but there was no indication that these bases had been used for large-scale decontamination.

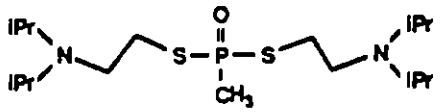
By contrast with HD, aqueous sodium hydroxide has been used as a standard method for the decontamination of bulk GB from munitions. The reaction yields sodium isopropyl methylphosphonate and sodium fluoride. It has been employed for demilitarization of the M55 rocket[18] and M139 and E139 bomblets,[19] among other applications. Once the GB has been hydrolyzed, the brine solution is dried prior to disposal. A voluminous literature[20-30] base has resulted for the testing for residual GB in the brine, in the stack emission, and in the dried salts. There are two standard methods for GB trace analysis, enzyme and GLC. Both require extraction of residual GB from the material of interest with a polychlorinated alkane. For the enzyme method,[23,24] which is more sensitive but less specific and subject to more interference, the extract is usually subjected to a preliminary TLC separation[31] followed by scraping-off of the spot, reaction with cholinesterase and by a pH, colorimetric or fluorometric measurement. The GLC procedure,[25,32-34] is less sensitive, but more specific (Section 8).

Because sodium hydroxide solutions produce hydrogen with the aluminum often accompanying the GB in munitions, less basic solutions have been investigated. One of these is aqueous sodium carbonate,[12,35] which is less corrosive for aluminum. The half life of GB in this solution was reported to be 8.5 seconds with a first order rate constant of 0.08 s^{-1} and a destruction efficiency of >99.9999%. The heat of reaction (ΔH) with 10% sodium carbonate

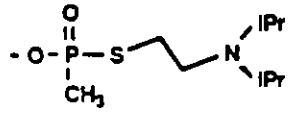
has been estimated to be -22 kcal/mole. This was shown to give a "safe" temperature rise of 2.58°C for an adiabatic process using 300% excess reagent (one pound of GB per seven gallons of 10% sodium carbonate.) Methods of analysis were essentially the same as those for hydroxide brines. Nmr analysis of spent 10% carbonate solutions indicate GA, GB, and GD destroyed to 99.5% in 5 minutes at room temperature (see Appendix).

While VX is more resistant to cleavage by bases than GA, GB, and GD, it has been decomposed with aqueous sodium hydroxide.[36] Decontamination of 12.5 gallons of VX by 150 gallons of 10% sodium hydroxide required 6 to 8 hours with air agitation at 25-30°C. This technique was recommended by Monsanto,[37] but the sulfur and nitrogen degradation products, including diisopropylaminoethanol are not commercially reusable.

Similar studies were reported by the Navy.[38] A total of 12.5 gallons of VX was decontaminated using 150 gallons of 10% aqueous sodium hydroxide (air agitated) in three stages (50 gallon addition, each stage). The solubility of VX was initially incomplete. The last two stages employed heated sodium hydroxide solutions. The time for "complete"decontamination was 6-8 hrs. The solubilization problem indicates that this method of decontamination will be unreliable unless the mixing process can be very adequately controlled. It must also be noted that if the reacting VX contains the "Bis impurity", the action of base will generate a refractory compound (see formula below) which undergoes further hydrolysis slowly. This refractory anticholinesterase is toxic by intravenous routes; the oral toxicity is considerably less. However, this material, in aqueous or alcoholic solution, is apparently not absorbed through the skin; no effects were found on application in water or alcohol to the backs of clipped rabbits.[47] The compound is crystalline when pure (mp = 138-140°C) and is infinitely soluble in water and ethyl alcohol; as such it is not a vapor hazard.

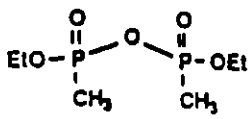


"bis"analog of VX



refractory anticholinesterase

In work done to support the Demil plan at the Tooele Army Depot[21] three decontamination procedures were evaluated for large scale destruction of VX. These included alconolic caustic, calcium hypochlorite, and chlorine gas in acidic media (acid chloronolysis). It was suggested than in addition to the two analogues discussed above, the base reaction also produces the "pyro" compound; structure shown below) by reaction of the O-ethyl methyl phosphonic acid anion (initial hydrolysis product of VX) with VX.



This product also hydrolyzed on standing with aqueous base. This study reports that incomplete reaction of VX with either hydroxide or calcium hypochlorite produced solutions which gave weak toxicological results (by intravenous injection) but that excess reagent produced solutions clean of any major toxicological response (rabbits and mice). The conclusion of these studies indicated that acid chloronolysis was the solution method of choice for large scale destruction of VX in Demil procedures.

Methods of analysis for residual VX in the brines and in the dried salts are similar to those for GB and involve extraction of agent followed by GLC (phosphorus and sulfur flame filters), or TLC, with enzyme analysis.[8, 21,39]

Sodium hydroxide also appears to be the decontaminant of choice for L. Nmr analysis show that treatment of L with 10% sodium hydroxide solution immediately evolves gas (acetylene) and produces a solution with >99.5% L destruction (no carbon signals present) in 5 minutes (See Appendix).

A number of other strongly basic sodium salts have been suggested[40] as substitutes for sodium hydroxide or sodium carbonate in the decontamination, including trisodium phosphate or sodium silicate, but they do not seem to have been studied in any detail.

4.1.3.2 Partly Aqueous and Nonaqueous Solutions

The main advantage in working in these media is that the agent is usually more soluble and hence should be more readily available for nucleophilic attack, other factors being equal. Yet the fact that partially or completely nonaqueous solutions have lower dielectric constants than water may slow the reaction. Also, there are often problems of toxicity and corrosivity connected with organic solvents. In the following examples, it should be noted that these reagents are preferred for small-scale decontamination, such as on skin, cloth, metal, or other surfaces.

Sodium sulfide, 15% in a mixture of glycerol, ethanol and water, required 20 hours at an ambient temperature to destroy HD.[6]

Sodium hydroxide in methanol reacts too slowly with HD to be effective, yet in ethanol, the half life is 11 hours.[14] While VX, like HD, is more soluble in alcoholic base, problems of flammability have lessened that decontaminant's use.[13] An effective skin decontaminant for HD was described by Steyermark,[41] which consists of a quaternary ammonium hydroxide or alkali metal hydroxide, alkoxide, or phenoxide in mixtures of dimethyl sulfoxide and water or alcohol. A mixture of 70% methyl cellosolve and 30% of a 50% aqueous sodium hydroxide solution [42] gave complete destruction of HD in 2 hours (verified by GLC) to yield thiodiglycol and sodium chloride. This agent has a relatively large capacity for HD decontamination and compared very favorably with other HD decontaminants.

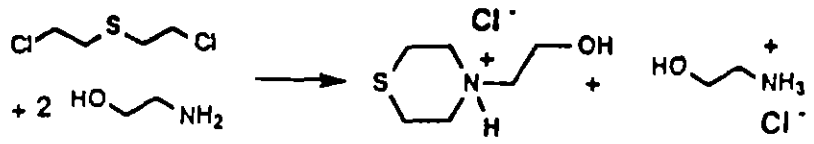
A number of multicomponent, strongly basic mixtures have been studied for the decontamination of HD, GA, GB, GD, L and VX. One of these is DS-2, patented by Jackson[43] as being effective, and relatively noncorrosive, and consisting of 70% diethylenetriamine, 28% 2-methoxyethanol and 2% sodium hydroxide. With this mixture, the half lives for HD, GB, and VX[44,45] were found to be 2.3 seconds, <30 seconds and <7 seconds, respectively, at ambient temperature. The products formed from HD included divinyl sulfide, which is somewhat toxic, but much less so than HD. In one report,[44] 25 cc of HD plus 1.33 quarts of DS-2 gave a 31% yield of divinyl sulfide in a very rapid reaction. Residual HD was determined via GLC. Other studies on DS-2 were made by Day[46] with HD, cyclohexyl methylphosphonofluoridate (GF) (GB analog) and VX on painted panels after standing overnight, and by Fielding[48] on various surfaces. Treatment was found to be effective for GB and HD, but somewhat less so for VX. The products from VX were tentatively identified as bis (2-diisopropylaminoethyl) disulfide,[44] presumably plus the O-ethyl methylphosphonic acid. For GB, the products are the same as those for hydrolysis in aqueous sodium hydroxide.

In work performed with DS-2 at Monsanto,[49] a thorough study was made on the function of the three components in the solution. It was postulated that the amine in DS-2 complexes with the sodium ion to give a superbase. Substitutes included crown ethers, polyethyleneimine and iminobis(propylamine). The 2-methoxyethanol in the standard DS-2 mixture was replaced as solvent by a variety of glymes in various formulations and the sodium hydroxide by lithium diethylamide. None of the substitute formulations was found to be markedly superior to DS-2, which gave 100% HD destruction at an ambient temperature in several minutes. Unfortunately, because DS-2 has a low sodium hydroxide content (2%), increased volumes (vs. HTH) must be used to obtain equivalent levels of decontamination. It is also corrosive to epoxy resins, neoprene, and wood.[40]

In studies made on the reaction of VX with ethanolamine, with hexyleneglycol added to give homogeneity, it was found that 70% of the VX remained intact after 2.5 hr at room temperature.[38]

Studies by the Navy[50] were made of benzyltrimethylammonium hydroxide in methanol as a decontaminant for small amounts of VX in the laboratory.

Monoethanolamine (MEA), an organic solvent, which is itself a relatively strong base, has been used for the decontamination of HD.[16] The use of MEA has a number of decided advantages[51,52] including: relatively high flash point, relatively non-toxic (TLV of 3 ppm), non-corrosive to metals, inexpensive, relatively stable, homogeneous reaction with HD, moderate heat of reaction and volume ratio of only 5:1 required. The reaction of HD and MEA is given by the equation:



The type of reaction represented by the above equation has received attention in the open literature,[38] but quantitative studies of products, kinetics and thermochemistry were not reported. A decided advantage of these systems is the absence of inorganic salts in the final disposition process. The products from HD, ie, N-(2-hydroxyethyl)thiomorpholine hydrochloride, monoethanolamine hydrochloride and small amounts of bis(hydroxyethylaminoethyl)sulfide, were incinerated at 900°C to give carbon dioxide, hydrogen chloride and various oxides of nitrogen and sulfur, which were collected in an 18% aqueous sodium hydroxide scrubber.[16]

The half life of this reaction was reported as being 11 min at 57°C and 40 min at 44°C.[38] The heat of reaction at 50°C was -40 kcal/mol. Above this temperature,the heat of reaction increased significantly and cooling was required. With a 5:1 v/v ratio of MEA to HD, the adiabatic temperature rises were from 50°C initial to 113°C final and from 65°C initial to 151°C final.

Studies have indicated that for chloroform solutions of various agents, reaction with MEA may yield a delayed violently exothermic reaction, especially in closed vessels. The hazard of a slowly appearing exotherm, which nevertheless results in a violent run-away reaction upon storage (reaction of MEA with solvent), is not an isolated instance in the history of stored materials resulting from disposal operations. Detailed methods and apparatus are being developed for safely eliminating the appearance of such unpleasant surprises.[38] Analysis of various systems are performed by computer-controlled adiabatic calorimetry with computer data-processing. Other approaches to the problem have been the previous use of differential thermal analysis (DTA) and differential scanning calorimetry (DSC), but the approach cited in the above reference develops much more complete information for analysis, if an actual problem exists. Detection of the problem should be adequately performed however, by DTA and/or DSC.

Several additional studies[51,52] led to the selection of MEA as a feasible decontaminant for HD. The compound has also been applied to the destruction of HD impregnated on charcoal[53]. When combined with 4-(N,N-dimethylamino)pyridine it has been employed for destruction of GB.[54]

4.1.3.3 Molten Salts

A novel technique for the destruction of chemical warfare agents involves the use of molten basic salts at elevated temperatures. In the method, first studied by Atomics International,[55-57] HD, GB, and VX in air, at feed rates of approximately 10 grams per minute, were passed through beds containing 90%

sodium carbonate and 10% sodium sulfate at 1000°C. The agents react according to the following equations:

$HD + 2\ Na_2CO_3 + 7\ O_2 \rightarrow Na_2SO_4 + 2\ NaCl + 6\ CO_2 + 4\ H_2O$

$VX + 3\ Na_2CO_3 + 20.5\ O_2 \rightarrow Na_3PO_4 + Na_2SO_4 + NaNO3 + 14\ CO_2 + 13\ H_2O$

$GB + 2\ Na_2CO_3 + 6.5\ O_2 \rightarrow NaF + Na_3PO_4 + 6\ CO_2 + 5\ H_2O$

The bench scale results were: HD off-gas <0.023 mg/m^3, particulate filter <30 ng, melt residue <30 ng/gm; GD off-gas <0.00049 ng/m^3, filter <50 ng, melt <100 ng/gm; VX off-gas gas <0.000085 mg/m^3, filters <1.5 ng, melt <3 mg/gm. These figures corresponded to agent destruction of 99.99999%.[58] Assay was *via* extraction followed by GLC-mass spectrometry for GB and HD or by enzyme analysis for VX.

The molten salt method has several problems, including the presence of phosphorus pentoxide particulates, requiring efficient particulate filters, and the presence of sodium chloride condensation in off-gas lines, requiring low temperatures for the molten salt.[59]

4.1.4 COMPLEXING AGENTS AND NUCLEOPHILES

4.1.4.1 Metallic Salts

These compounds customarily are employed in solutions closer to neutrality than are the bases of Section 3 above and are frequently much less corrosive. Various metal ions have been observed to increase the hydrolysis rates of GB in water,[60-65] especially those of copper (II), uranium (VI), zirconium (IV), thorium (IV), and molybdenum (VI). Only a few of these systems have actually been translated into useful decontamination procedures. In one,[45] VX and GB on sateen were treated with 0.1 M uranyl nitrate and 0.1 M thorium nitrate solutions; neither was too effective. In another report,[66] involving VX in solution, 95-98% was destroyed in 30 minutes with either zirconium (IV), nitrate or copper (II) nitrate and tetramethylethylenediamine. Also satisfactory was uranium (VI) dioxybis(5-sulfo-8-hydroxyquinoline), with half life for GB of 2.8 minutes at pH 10 and 24 minutes at pH 7.[67] Various metal salts complex with HD without actually decomposing it, including mercury (II) perchlorate.[68] These have been used to impregnate clothing, but are deactivated by perspiration.

Interest in decomposition of agents with metallic complexes has returned with investigations involving several promising compounds.[69]

4.1.4.2 Alpha Nucleophiles

While hydroxide anion readily attacks electrophiles such as HD, GA, GB, GD and VX, even more rapid reactions are given by various alpha nucleophiles, even though they are less basic. The enhanced reactivity is related to the

presence of an unshared electron pair on the atom next to the one bearing the negative charge, which decreases charge repulsion during interaction. In this group are anions of hydroperoxides, hypochlorites, oximes, and hydroxamic acids, with most literature references involving GB and VX.[60,70-74] While a number of these reactions have very favorable kinetics, as measured in the laboratory, only hypochlorites appear to have been used for large-scale decontamination and these properly fall under the heading of oxidants, considered below. In one report,[75] a mixture of sodium hypochlorite and sodium perborate was used for HD, but no rationale was given. In a hypothetical exercise,[13] a search was made for a hydroxamic acid that would decontaminate 400 gm of VX from a munition by dissolution in 1200 L of a 0.2 M aqueous solution of the hydroxamic acid at pH 7 to 9 to give a final agent concentration of 10^{-7} to 10^{-8} M after 1 hour. The sought-after acid was not found. A number of promising alpha nucleophiles have been synthesized by Reiner, which react rapidly with diisopropyl phosphonofluoridate (DFP, a G-agent simulant) including a-oxominovaleronitrile, ethylenediaminetetracetohydroxamic acid, amylose oxime, and pentafluoro-benzaldoxime.[76]

Besides alpha nucleophiles, bidentate nucleophiles such as pyrocatechol and pyrogallol anions[77-81] were found to hydrolyze organophosphates rapidly. Here, too, promising results in the laboratory have not been turned into practical systems.

Sodium thiosulfate reacts rapidly with HD,[82] but neither this reaction, nor one involving hydrolysis of GB at pH 7.6 in the presence of pyridinium bases,[83] has been applied to bulk quantities of agents.

4.1.4.3 Micellar Nucleophiles

In this group are oximes containing a large aliphatic moiety, which tends to concentrate on the surface of solution, where more favorable concentration effects should enhance organophosphate hydrolysis. As an example, the half life or VX in a pH 9.3 solution containing dodecylpyridinium-3-aldoxime iodide (10^{-3} M) was 40 seconds.[84]

4.1.5 OXIDANTS

4.1.5.1 Halogen

4.1.5.1.1 Calcium Hypochlorite

Of the agents under consideration in this report, two, HD and VX, contain sulfur moieties that are readily subject to oxidation. One of the first substances[6] used for the destruction of HD was "bleach", which is normally found in three forms: a 5% aqueous sodium hypochlorite solution (Clorox, Purex, etc.), chlorinated lime (a solid with the approximate formula CaClOCl) and calcium hypochlorite (HTH, with the formula $Ca(OCl)_2$). The last named, having the

highest percentage of available chlorine, is the form most often used for current decontamination.

The reaction of calcium hypochlorite with HD has been conducted in a variety of media.[14] With solid reagent, the reaction may be violently exothermic.[85] With hypochlorite in an aqueous slurry, the reaction is more easily controlled. This mixture has been recommended for the detoxification of buildings, ground, and other large-surface areas.[86-89]

While the reaction varies with the proportion of reactants and temperature, a proposed equation[15] for the maximum consumption of bleach is:

$$(ClCH_2CH_2)_2S + 14\ OCl^- \rightarrow SO_4^= + 16\ Cl^- + 4\ CO_2 + 4\ H^+ + 2\ H_2O$$

With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of mustard may be produced.[90] Nmr analysis of the oxidation with excess bleach show conversion into numerous (estimated 20) products in greater than 99.5%, none of which were mustard (See Appendix). Toxicological test on mustard decontaminated with bleach show no toxic effects.

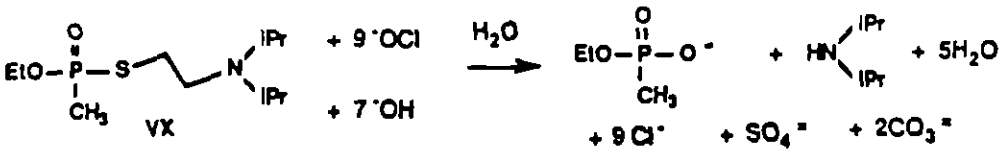
As HD is relatively insoluble in water, the reaction with aqueous calcium hypochlorite is a heterogeneous one and rates of decontamination have not been studied.[15] Nevertheless, several kinetic investigations have been made in dilute homogeneous solutions at various pH values.[91,92] In actual decontamination of HD with calcium hypochlorite,[93] scaled-down amounts, corresponding to ratios of 11.7 lb.of HD to 100 lb of HTH in 108 gal. of water were stored for several days at an ambient temperature, treated with sodium thiosulfate to remove excess hypochlorite and extracted with hexane. The extracts were submitted to GLC with sensitivity of 1 ppm of HD in hexane and results indicated essentially complete decontamination. The equation given for the reaction was:

$$(ClCH_2CH_2)_2S + 7\ Ca(OCl)_2 + 2\ Ca(OH)_2 \rightarrow CaSO_4 + 8\ CaCl_2 + 4\ CO_2 + 6\ H_2O$$

A bleach slurry was found to give complete decontamination of HD on Navy landing craft.[1] The agent HD is determined in bleach solution[33] *via* extraction and subsequent GLC (Section 8).

In order to speed up reaction, suspensions have been made of bleaching powder in organic solvents. One such solvent was carbon tetrachloride,[15] which was found to be superior to aqueous bleach paste, but was still slow because of the heterogenous nature of the reaction. Another example involved the use of 8% calcium hypochlorite in a mixture of 76% water and 15% chlorinated hydrocarbon, with 1% alkylbenzenesulfonate emulsifier.[94] Reaction occurred at the phase interface and theoretically, the system could be improved *via* inclusion of a phase transfer catalyst.[13] More efficient are the organic chlorinating agents discussed below:

Calcium hypochlorite has also been applied to the decontamination of VX, the reaction being given by the equation:[95]



The reaction is rapid, with a half life of 1.5 minutes at pH 10. It has been used for the demilitarization of VX in the CAMDS Project at Tooele Army Depot,[21] but it was considered to be less effective than is acid chlorinolysis. The major determinant of the transformation is that the pH is critical and toxic solutions can be formed if the pH drops to a value below 11 (see discussion above).

The reaction is highly exothermic[38], with an experimentally determined value of -675 kcal/mol and a first order rate constant of 0.01 s^{-1}. The rise in temperature can be calculated from the equation:

rise in°C = (moles VX)(175)/gal.10 % HTH

Initial results with extraction of trace amounts of VX from hypochlorite gave poor recoveries[96,97]. The current analytical procedure[33] is much more satisfactory (Section 8).

The reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation, it offers no advantage over aqueous sodium hydroxide.[137]

Self-destructing HTH solutions to limit corrosion have been prepared, with half lives of approximately 100 seconds. They are named ASH and SLASH,[98] contain citrate to remove excess active chlorine and have been used for biological agents.

4.1.5.1.2 Sodium Dichloroisocyanurate

Similar in action to HTH is sodium dichloroisocyanurate monohydrate (Fichlor, CDB-63), which possesses considerable aqueous stability and solubility (1 M/L) and has been used for laboratory-scale decontamination of VX.[99] The compound was reported for destruction of HD, GD, and VX on paint surfaces[100] and the test results were compared with those for other decontaminating agents. As with sodium hypochlorite, the stability of sodium dichloroisocyanurate in aqueous solution is pH dependent.[101] Because of its favorable characteristics relative to calcium hypochlorite, there is a current interest in Fichlor.[102]

4.1.5.1.3 Chloramine B, Chloramine T and NBO

Two other water-soluble active chlorine compounds of interest are Chloramines B and T. As compared to HTH, they have the advantage of greater stability[88,89] and less corrosiveness when applied to skin, but being more expensive, are not recommended for large-scale operations. Theoretical studies have been made on N-chlorinated compounds by Higuchi and coworkers.[103] In general, the weaker is the acidity of the NH base, the more stable the N-chloro compound. They react readily with tertiary amines and a number of them have been suggested as decontaminants for VX.[13] The products of reaction of chloramine B with HD include bis(2-chloroethyl) sulfoxide and the sulfilimine $C_6H_5SO_2N{=}S(CH_2CH_2C1)_2$.[104,105] The proportion of the former increases with increasing water content.

An aqueous mixture containing 3-bromo-4,4-dimethyl-2-oxazolidinone (NBO) and cetyltrimethylammonium chloride in a bicarbonate/carbonate buffer has been studied for the decomposition of HD and VX as well as GD.[106] The solubility of NBO in the mixture is 0.14 M at 19°C. A 0.01 M NBO solution containing 0.0034 M HD gave < 1% HD (GLC) at 10 min (half life of 0.2 min). For VX and the reagent,at a 1:10 mole ratio,the half life of the VX was 0.2 min. Studies with GD (and by analogy GB)indicated that both hydrolysis and attack by reagent were occurring,with an agent half life of 0.5 min at a 1:1 mole ratio. Unfortunately,stability problems in solution have prevented greater use of this decontaminant.

4.1.5.1.4 Dichloramine B, Dichloramine T, DANC, and Other Water-Insoluble Active Chlorine Compounds.

This group of compounds is soluble in many of the solvents in which HD and VX are soluble. However, they are unstable in varying degrees to sunlight and to moisture.[107] The dichloramines have been applied in carbon tetrachloride solution,[108] in salves,[108] with inert solids such as kieselguhr or talc, or with alkali or alkaline earth carbonates or bicarbonates.[109]

Other examples for this group include N-chlorosaccharin,[13] N-chloro-succinimide,[13] N-chloracetamide,[110] N-chlorophthalimide,[110] bis (2,4,6-trichlorophenyl)dichlorourea,[111] and N-(2,3,6-trichlorophenyl) N-chlorobenzamide.[107]

Various other active chlorine compounds have been investigated.[112,113]

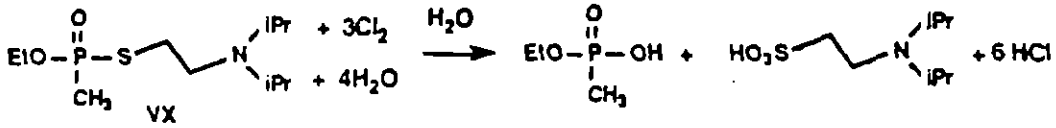
With N-chlorosaccharin, it was predicted[13] that at pH 8.6 in aqueous solution the half life of VX would be 10^{-4} seconds, but low water solubility among other factors, prevented application of the compound.

One formulation that was used extensively in the past was DANC,[14,15] a 7% solution of 1,1-methylenebis(3-chloro-5,5-dimethylhydantoin)(S-210) in tetrachloroethane. Other formulations[15] include: S-210 10.3%, tetrachloroethane 67.3%, barium hydroxide octahydrate 2.8%, Aristowax 1.6%,

and S-210 1%, tetrachloroethane 2.9%, Spar 201 4%, water 7%, remainder oil. In aqueous solution, S-210 reacts with HD to give a sulfilimine derivative.[95] Because of the high toxicity of tetrachloroethane and its corrosive effect on painted surfaces and rubber, DANC has become obsolete.

4.1.5.1.5 Chlorine and Chlorine Dioxide

Chlorine has been used as a large-scale decontaminant for VX, based upon earlier laboratory studies (half life 1.2 minutes at pH4).[114] In the actual procedure carried out at the Tooele Army Depot,[115] 100-pound batches of VX from munitions are dissolved in 1.5 N hydrochloric acid (1:3 v/v) and chlorine is added to a green color. Reaction is rapid and strongly exothermic. Samples are quenched with sodium hydroxide or sodium carbonate and extracted with dichloromethane. Residual agent (3 µg/L) is determined via fluorimetry,[116] TLC and an enzyme assay[23] or GLC.[117] The destruction efficiency was determined to be 99.999999%. The reaction is:



Also found among the products was dicyclohexylurea from the dicyclohexylcarbodiimide stabilizer in the VX. The solution from the chlorinolysis was converted to drum-dried salts.[118]

Chlorine dioxide reacts with VX to give carbon dioxide, carbonyl sulfide, sulfate ion, phosphonic acid and diisopropylamine.[119] As with chlorine, kinetics are very favorable, but the explosive nature of the gas would tend to preclude large-scale work.

4.1.5.2 Other Oxidants

An early oxidant used for the destruction of HD was potassium permanganate in acetone,[6] for cleaning of metallic instruments. Neutral permanganate was reported to completely detoxify (enzyme-assay) VX at a 20:1 molar ratio.[119] Among the products were ethyl methylphosphonic acid, N,N-diisopropylformamide, sulfate ion and gelatinous manganese dioxide, which along with unreacted permanganate, presented disposal problems. When VX was reacted with permanganate in highly basic solution,[13] the products formed indicated that hydrolysis predominated over oxidation.

Potassium peroxydisulfate, in combination with a silver ion catalyst, has been suggested for the decomposition of VX,[13] but no experimental work seems to have been done.

Oxidation of mustard with concentrated nitric acid cleanly produces >99.55 mustard sulfoxide (See Appendix).

Peracetic acid gave unimpressive results with GB and VX on sateen swatches.[45]

Various free radical systems were studied for oxidation of HD, GB, and VX, but it was concluded that the approach showed little promise.[120,121]

Novel oxidations of various agents with organic iodo compounds have been reported.[122,123,124]

4.1.6 PHOTOCHEMICAL METHODS

Little work has been done using this approach. Both HD and VX contain sulfur atoms that are subject to oxidation. One system that has been proposed for VX involves cold aerial photooxidation with photosensitizers such as Rose Bengal.[13,125] The decays in GB and VX clouds as they travel downwind, due to photolysis, hydrolysis and oxidation, have been reported.[126]

4.1.7 PHYSICAL COLLECTION

Physical collection removes the agent from one location to another without actually destroying it. It is primarily of value for the decontamination of surfaces or the removal of agent from water. Washing surfaces with water, water with detergent, or ethanol, has been used for decontamination.[127]

An early method of physical collection involved adsorption of various toxic chemicals.[128] A more recent technique is that of reverse osmosis[129] for removal of GB and VX from water with cellulose acetate and polyamide membranes. Agent concentrations were significantly reduced, but not always to a permissible level.

Ion exchange resins have been employed to remove small amounts of VX from hypochlorite brines,[96] but this was an analytical technique rather than a method of decontamination. Amberlyte-15 resin (Rohm and Haas Corporation) was studied for the removal of GB, VX, and HD from air.[135] Basic resins absorbed GB and possible hydrolytic products, then catalyzed the hydrolysis of GB.[131]

A review of ion-exchange methods reported for decontamination,with proposals for future work,was published in 1983. Among the recommendations were ultra-fine resin-zeolite slurries as general-purpose noncorrosive surface decontaminants and mixed bed cation-anion exchangers for potable water decontamination.[132]

Aqueous charcoal slurries (23-28%) in water, plus corrosion inhibitors and antifreeze compounds, have been mentioned for decontamination.[40]

4.1.8. ANALYTICAL PROCEDURES FOR STANDARD DECONTAMINATION METHODS

The standard method for the determination of residual GB in 18% sodium hydroxide solution requires initial adjustment of the pH to 5.0 with dilute sulfuric acid,followed by extraction with chloroform,preconcentration of the extract using Chromosorb 106 and GLC analysis.The column type is DB-210 bonded-phase fused silica capillary,15 m long by 0.53 mm ID, with a 1.0 um coated thickness of the stationary phase.The detector mode is phosphorus specific and the detection limit is 6.3 ppb.[33] An essentially identical procedure is used for the determination of GB in scrubber solutions and in sodium carbonate brines with detection limits of 4.8 ppb and 6.3 ppb respectively. Gas chromatographic analysis of GB also has been reported using a DB5 megabore column 30 m by 1.5 µ (J & W Scientific) with a detection limit of 0.05µg/mL of injected sample.[34]

A colorimetric technique for GB using o-dianisidine and perborate has a reported detection limit of 0.5 µg/ml,while an autoanalyzer procedure utilizing acetylcholineesterase and 5,5-dithiobis-2-nitrobenzoic acid claims a value of 0.25 ng/mL for the agent in an air stream.[34]

The agent HD is determined in bleach solution according to the following procedure.[33] Excess bleach is neutralized with aqueous sodium arsenite, the end point being determined bipotentiometrically.Extraction is made with chloroform followed by preconcentration on Tenax-GC. The gas chromatography column is DB-210 bonded-phase,fused silica capillary, 15m long by 0.53mm ID, with a 1.0µm coating thickness of the stationary phase. The detector is sulfur specific, with a detection limit of 39.4 ppb.

The analysis of residual VX in hypochlorite requires an extraction prior to GLC. Initially, *n*-hexane was the extractant, with a detection limit of 0.6 µg/mL, but recovery was poor.[96,97] The current method involves extraction with chloroform after a preliminary removal of excess hypochlorite with arsenite (see HD analysis above) and increase of pH to 10.0. Preconcentration requires adsorption on Chromosorb 106 and conversion to a fluoro compound similar to GB by reaction with silver fluoride.The chromatographic column and detector are the same as those for GB and the detection limit is 11.4 ppb.[33] A DB 608 column has been suggested for analysis of VX[34] as well as a DB-5 megabore column (30m, 1.5µ, J&W Scientific) with a detection limit of 1µg/mL for the latter.

Several proposals have been made for the analysis of L in trace amounts. In one (E.W.Sarver, Unpublished Results, 1974), the agent is reacted with 1,2-ethanedithiol to give 2-(β-chlorovinyl)-1,3-dithioarsenole, which is submitted to GLC.Another proposal involves a preliminary separation *via* high performance liquid chromatography coupled with amperometric assay, with an estimated detection limit of 1 ppm.[138] Preliminary studies have been made (S.Hallowell,Unpublished Results,1976) of the titration of Lewisite with sodium 1,2-propanedithiol-3-sulfonate and a sulfide electrode.

4.1.9 CONCLUSION

Extensive decontamination experience and comprehensive data bases reviewed above have underwritten huge demilitarization projects in the past including GB-filled M55 rockets, and M139 and E139 bomblets, as well as research level decontamination protocol's utilized here at CRDEC and in other U.S. Army and free world instillations. An extensive evaluation of various of the above decontamination methods with respect to reliability, simplicity, safety and cost was made by the Jet Propulsion Laboratory.[139] In all cases, decontamination and disposal projects for agent-filled munitions were executed safety, without untoward incident, and in total compliance with every prevailing environmental and human safety stricture and concern at the time of the operation. As can be seen from the analytical data reviewed the thermodynamics, kinetics and product analysis documentation is extensive and has improved in recent times by advances in analytical hardware, as exemplified by the nmr data reported in the Appendix of this document. These modern analytical tools have by-in-large confirmed the archival data. These and other facts enumerated in detail in this document provide ample evidence that existing decontamination protocols and procedures are safe, scientific, and result in the total destruction and detoxification of chemical agents.

4.1.10 LITERATURE CITED

1. Fielding, G. H. et al. NRL Report No. P-2914. Decontamination of Landing Craft at San Jose Island. Naval Research Laboratory, July 1946.

2. Herriot, R. M. and Anson, M. L. OSRD 653, NRDC Series 275. Effect of Detergents and Related Compounds on the Solubility and Rate of Solution of RHS. June 1942.

3. Holst, G., Comparison of Pyridine, Ethyl Alcohol, Acetone as Solubilizing Agents. Acta Chem. Scand. 12, 1042 (1958).

4. Edgewood Proving Ground Report on Test 689. Effectiveness for Decontamination of Hot and Cold Water with and without Detergents. December 1947.

5. Fielding, G. H. NRL Report C-3240-70A/52CbM. Decontamination of Ships. Operation Leroy. Naval Research Laboratory. May 1952.

6. Chemical Warfare Service Report No. Z-197. The Cleaning of Objects Contamination with Yperite. Washington, D.C. May 1918.

7. Williamson, C. E. and Witten, B. EATR-4490. Reaction of Some Nitrogen and Sulfur Mustards in Detergent Micelles. February 1971.

8. Crabtree, E. V. and Sarver, E. W., EC-SP-76021. Review of Analytical Procedures for GB, VX, and their Degradation Products. January 1977.

9. Wilson, R. E. et al. Solubility and Rate of Hydrolysis of Mustard Gas in water. J. Am. Chem. Soc. 44, 2867 (1922).

10. Larsson, L. the Alkaline Hydrolysis of Isopropoxy - Methyl - Phosphoryl - Fluoride and Some Analogs. Acta Chem. Scand. 11, 1131 (1957).

11. Epstein, J. et al. The Kinetics and Mechanisms of Hydrolysis of Phosphonothiolates in Dilute Aqueous Solution. Phosphorus 4, 157 (1974).

12. Davis, G. T. et al.,EC-TR-76101. Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components. March 1977.

13. Davis, G. T. et al., ARCSL-TR-78028. Search for a Noncorrosive Decontaminant for VX and for Application in Demilitarization Operations. July 1987.

14. Mankowich, K. et al. EASP-300-5-Pt-2. History of Research and Development of the Chemical Warfare Service through 1945. Decontamination of Chemical Agents. Part II. September 1970.

15. Block, F. and Davis, G. T. ARCSL-TR-79002. Survey of Decontamination Methods Related to Field Decontamination of Vehicles and Materiel. October 1978.

16. Brankowitz, W. R. ARCSL-TR-77051. Demilitarization of Mustard Agent (HD) at Fort McClellan, Alabama April 1978.

17. Reichert, C. Defence Research Establishment Suffield Ralston. DRES-TN-329.Study of Mustard Destruction by Hydrolysis.July 1975

18. Edwards, B. A. DPG-SS-C130A. Caustic Immersion Demilitarization of M55 Rocket Residue. February 1974.

19. Mohammed, A. M. DPG-FR-C150B. Demilitarization of M139 and E139 Bomblets at Dugway Proving Ground, Utah. Use of Sodium Hydroxide Solution. April 1978.

20. Davis, P. M. et al. EC-TR-76079. Chemical and Thermal Methods for Analysis of GB Demil Brines and Spray Dried Salts. February 1977.

21. Thomas, G. W. DRCPM-DRD-TR-72015. Demil Plan Operation of the CAMDS at Tooele Army Depot. Inclosure No. 10. Agent Destruction System Testing and Reliability Data. March 1977.

22. Rinehart, D. ARCSL-TR-77031. The Determination of GB Emissions from Rocky Mountain Arsenal M34 Spray Drier. December 1977.

23. Hess, T. L. USAEHA Rep AD No. 717558. An Automated Method for Measurement of Nanagram Quantities of Organophosphorus Poisons. November 1970.

24. Tomlinson, D. H. and Feller, H. L. ED-TR-76045. Improved Auto Analysis for Nanogram Quantities of Organophosphorus Agents GB and VX. May 1976.

25. Belcher, D. W. Spray Drying of War Gas Residues. Chem. Eng. Prog. 73, 101 (1977).

26. Gilson, N. C. Defense Research Establishment, Ottawa. DREO-693. Rapid Sensitive Gas-Liquid Chromatographic Methods for Analysis of HD, GF, and VX(U). June 1974. RESTRICTED Report.

27. Epstein, J. et al. EC-TR-76009. On the Mechanism of GB Formation in Spray Drying of GB Contaminated Brine Solutions. November 1975.

28. Taczak, W. J. et al. NSWC/DL-TR-3313. The Detection and Tracking of Stack Effluent with a Forward Looking IR Image Sensor. June 1975.

29. Barrett, J. W. et al. Southern Research Institute Quarterly Progress Report No. 8, SORI-EAS-75-417. Contract DAAA 15-73-C-0227. Investigation of Contamination from C-Agent Demil Plants and Determination of Effects on Real Time C-Agent Detection System. September 1975.

30. Goodson, L. H. and Jacobs, W. B. Midwest Research Institute Contract No. DAAA15-74-C-0069. Final Report. Solution Sampling Enzyme Alarm Studies (Spray Drier Studies) Analytical Chemistry. 1 December 1975.

31. Ludemann, W., and Sass, S. EC-TR-75062. Detection and Identification of Chemical Agents Using Spot Tests in Conjuction with TLC (U). November 1975. CONFIDENTIAL Report.

32. Fisher, T., et al. EC-TR-76080. Gas-chromatographic Methods for Analysis of Trace Quantities of GB and Associated Compounds (Demil of Effluent, Brine, Dried Salts, Munition Exudates). September 1976.

33. Smith, J. E. Southern Research Institute Contract No.DAAK11-82-C-0162 Analytical Methods Development.Vol.2.Standing Operating Procedures.Final Report.December 1985.

34. Fleming, E. H. Battelle Research Institute Contract No.DAAL03-86-D-0001C Summarization,Documentation,and Compilation of Current and Appropriate Procedures for the Chemical Analysis of CW Agents,Their Degradation Products and Selected Simulants.August 27,1987.

35. Rinehart, D. and Deiner, A. EO-TR-77008. Method of Analysis for Determination of Isopropyl Methylphosphonofluoridate (GB) in Carbonate Brines. June 1977.

36. Childers, C. D. Technical Memorandum W-15167. Decontamination of Bulk Quantities of VX with NaOH-Aqueous Solution. U.S. Naval Weapons Laboratory. Dahlgran, Virginia. August 1967.

37. Hedley, W.H., et al. Monsanto Research Corp. MRC-DA-476. Contract DAAA15-74-C-0073. Final Report. Disposal of Detoxified Chemical Agents. April 1977.

38. Yurow, H. W. and Davis, G. T. ARCSL-TR-81080. Decontamination and Disposal Methods for Chemical Agents.A literature Survey.November 1982.

39. Stutz, M., and Sass, S. EC-TR-76091. Collection and Sampling of Materials and Preparation for Identification and Other Analysis. June 1977.

40. Ashcroft, H. P., and Parker, D. T. DTC-71-713. Effect of Chemical and Biological Agents and Decontaminants on Equipment (U). 1978. SECRET Report.

41. Steyermark, P. R. Composition for Decontaminating Chemical Warfare Agents. (Grace, W. R. and Co.) USPatent 3,810,842;14 May 1974. C.A.81, 137872C (1974).

42. Davis, P. M., et al. ARCSL-TR-79004. Decontamination Solution for the Disposal of Identification and Training Sets. April 1979.

43.. Jackson, J. B. CWLR 2368. Development of Decontamination Solution DS-2. April 1960.

44. Davis, G. T. et al. EC-TR-75024. Studies on the Destruction of Toxic Agents VX and HD by the All-Purpose Decontaminants DS-2 and CD-1. May 1975.

45. Sturgill, R. A., et al. Litton Ind. GB-67-2378-6.1. Contract DA18-035- AMC-279A. Final Report. Methods and Material for Personnel and Equipment Decontamination. Book 1. Final Report for Task No. 24 on Collective Protection Against CB Agents. November 1970.

46. Day, S. E. and Gendason, P. ED-TR-74057. Laboratory Evaluation of the Decontaminating Effectiveness of DS-2 and SBT Slurry Against Agents on Painted metal. November 1974.

47. Michel, H. O.; Epstein, J.; Plapinger, R. R.; Fleisher, J. H. CRDLR 3135. EA2192, A Novel Anticholinesterase (U) Chemical Research and Development Laboratories Technical Report. May 1962.

48. Fielding, G. H. Report No. NRL-6191. Field Decontamination Studies with Chemical Warfare Decontamination Solution DS-2. Naval Research Laboratory. Washington, D.C. December 1964.

49. Richardson, G. A. Monsanto Corp. EACR 1310-17. Contract No. DAAA15-71- C-0508. Final Report. Development of a Physical Decontamination System. August 1972.

50. Brumfield, J. L., and Rumuly, D. L. NWL-TR-2513. The Reaction of VX with Benzyltrimethylammonium Methoxide.September 1970.Confidential Report.

51. Pistritto, J. and Eng, L. Edgewood Arsenal Letter Report. EACL 28 Research Investigations Concerning the decontamination of H/HD in Toxic Gas Sets. March 1974.

52. Davis, P.M., and Sass, S. Edgewood Arsenal Letter Report. Incineration Studies of a Solution of Detoxified Mustard (HD) - Monoethanolamine (MEA) Waste. December 1974.

53. Rosenberg, S. Nat. Tech. Info. Service AD Report AD-A042499. Detoxification of War Gas I.D. Sets Containing Charcoal Impregnated with Chemical Agent. 1977.

54. Cowsar, D. R. Southern Research Institute Report No. SORI-3808-4. Contract DAAA-15-77-C-0015. Final Report. Study of Reactive Materials for Development of New Protective Concepts. January 1978.

55. Yosim, S. J., et al. Rockwell Int. Atomics Int. Div. Contract DAAA15-74- C-0174. Final Report. Modification P00003. A Feasibility Study for the Disposal of Neutralized GB by the A.I. Molten Salt Combustion Process. June 1975.

56. Atomics Int. Div. Rockwell Int. Contract DAAA-15-74-C-0174. Final Report. Modification P00001. A Feasibility Study of Disposal of War Gas ID and Training Kits by A.I. Molten Salts Combustion Process. February 1975.

57. Rockwell Int. Atomics, Int. Div. Contract DAAA-15-74-C-0146. Final Report. Disposal of Obsolete War Gas ID and Training Sets by AI Molten Salt Combustion Process. Vols I and II. August 1976.

58. Dustin, D. F., et al. EM-TR-76099. Applications of Molten Salt Incineration to the Demilitarization and Disposal of Chemical Materiel. February 1977.

59. Kraybill, M. S. ARCSL-SP-77009. A Compendium of Molten Salt Combustion Studies. December 1977.

60. Larsson, L. Studies on the Chemical Reactivity of Organic Phosphorus Compounds. Sven. Kem. Tidskr. 70,405 (1958).

61. Wagner - Jauregg, T., et al. Model Reactions of Phorphorus - Containing Enzyme Inactivators. IV. The Catalytic Activity of Certain Metal Salts and Chelates in the Hydrolysis of Diisopropyl Fluorophosphate. J. Am. Chem. Soc. 77,922 (1955).

62. Courtney, R. C., et al. Metal Chelate Compounds as Catalysts in the Hydrolysis of Isopropyl Methylphosphonofluoridate and Diisopropyl Phosphonofluoridate. J. Am. Chem. Soc. 79, 3030 (1957)

63. Epstein, J. and Rosenblatt, D. H. Kinetics of Some Metal Ion Catalyzed Hydrolyses of Isopropyl Methylphosphonofluoridate (GB) at 25°C. J. Am. Chem. Soc. 80, 3596 (1958)

64. Gustafson, R. L. and Martell, A. E. A Kinetic Study of the Copper (II) Chelate Catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate. J. Am. Chem. Soc. 84, 2309 (1962).

65. Ploetze, E. Problem of Defense Against Chemical Warfare Materials. Explosivstoffe 12, 219 (1964).

66. Cogliano, J. A., and Braude, G. L. W. R. Grace. RES-69-61. Contract DA 18-035-AMC-287(A). Final Report. CW Agent Decontamination by Metal Salts and Organometallic Compounds. December 1969.

67. O.Connell, J. J., and Kwan, C. S. USAF Eglin Contract to Monsanto AD39-5943. Final Report. Chemical Warfare Decontamination by Catalyic Hydrolysis. February 1968.

68. Sharkley, L., et al. W. R. Grace Report No. RES-69-31. Contract DA18- 035 AMC-287(A). Quarterly Progress Report No. 19 Research and Feasibility Studies on Clothing Decontamination. June 1969.

69. Ward, J. R., and Hovanec, J. W. "On the Mechanism of Sarin Hydrolysis Catalyzed by Transition-Metal Ions", CRDEC-SP-85006, June 1985, page 29-33; Albizo, J. M., and Ward, J. R. "Hydrolysis of GD and VX by 0.05M/0.10M Copper (II) - N,N,N',N'-Tetramethylethylenediamine (TMEN)", CRDEC-SP-87008, June 1987, page 105-109.

70. Hackley, B. E., et al. Acceleration fo the Hydrolysis of Organic Fluorophosphates and Fluorophosphonates with Hydroxamic Acids. J. Am. Chem. Soc. 77, 3651 (1955)

71. Demek, M. M., et al. Hydroxamic Acid Catalyzed Hydrolysis. USPatent 3,068,072. December 11, 1962. C. A. 58,10660 (1963).

72. Epstein, J., et al. Chlorine Catalyzed Hydrolysis of Isoprpoyl Methylphosphonofluoridate (Sarin) in Aqueous Solutions. J. Am. Chem. Soc. 78, 4068 (1956).

73. Swidler, R., et al. The Kinetics of the Reaction of Isopropyl Methylphosphonofluoridate (Sarin) with Substituted Benzohydroxamic Acids. J. Am. Chem. Soc. 81, 327 (1959).

74. Stolberg, M., et al. CWLR 2285. The Reaction of VE with Oximes and Hydroxamic Acids. August 1959.

75. Vogel, C.I.B. A New Hypochlorite Preparation. Chem. Prod. 4, 40 (1941).

76. Reiner R., et al. The Decontamination of Surface Contaminated with CW Agents and Detoxification of agents Injected in organisms. Bundesministerium Der Verteidigung Bonn (West Germany) Wehrtechnik. BMVG-FBWT-74-6. 1974.

77. Jandorf, B. J. MLRR 81. Chemical Reactions of G Agent in Neutral Solution. Part II. Reaction with Mono and Polyphenols. September 1951.

78. O'Neil, J. J., et al. MLRR 160. Isolation of Reaction Products of GB with Amines, Hydroxylamine and Catechol. February 1953.

79. Higuchi,T. U. of Wisconsin Semi-annual Report. Contract DA 18-108-AMC-88(A). Molecular Catalysis and Interactions in aqueous Solutions. July 1963.

80. Epstein, J., et al. Reactions of Isopropylmethylphosphonofluoridate with Substituted Phenols. J. Am. Chem. Soc. 86, 3075, 4959 (1964).

81. Epstein, J., et al. Kinetics of the Reaction of Isopropyl Methylphosphonofluoridate with Catechols at 25°C. J. Am. Chem. Soc. 78,341 (1956).

82. Benes, J. and Weidenthaler, P. The Mechanism of the Reaction of Dichloroethyldisulfide with Sodium Thiosulfate. Chem. Zvesti 11, 324 (1957) CA 51, 16227 (1957).

83. Grochowski, J. W., et al. Hydrolysis of DFP and Sarin in the Presence of Pyridinium Bases and Some of Their Oxides. Biul. Wojsk. Akad. Tech. 14, 93 (1965) CA 65, 3685 (1966).

84. Epstein, J., et al. Micellar Acceleration of Organophosphate Hydrolysis by Pyridinium Aldoxime Type Surfactants. J. Org. Chem. 43,2816 (1978).

85. Lipscomb, A. G. The Reaction Between 2,2'-Dichlorodiethyl Sulfide (Mustard Gas) and Bleaching Powder. Analyst 65, 100 (1940).

86. Drager, H. Destruction of Toxics in Industrial Establishments. Dragerhefte 2210 (1932).

87. Renwanz, G. Detoxification of Buildings Contaminated with Mustard Gas (Bis(chlorothyl)sulfide). Gasmaske 7,1 (1935)

88. Weidner, D. The Destruction of Mustard Gas. Gasschutz and Luftschultz 5, 133 (1936).

89. van Giffen, H. J. and van Bronkhorst, W. A. The Cleaning up of Streets and Public Squares Contaminated with Mustard Gas. Pharm. Weekbl. 74, 102 (1937).

90. Buswell, A., et al. The Chemistry of Mustard Gas as a Water Contaminant. National Defense Research Committee of the Office of Scientific Research and Development, Informal Report 65, Section 9-3-2. August 1943.

91. Holst, G. The Reaction of Bis (2-chloroethyl) Sulfide (also the Oxidation Products Sulfoxide and Sulfone) with Hypochlorite in Pyridine - Water Solution. Sven. Kem. Tidskr. 53, 319 (1941) CA 36,6881 (1942)

92. Eskanow, K. and Jachlewski, Z. Studying the Reaction of β,β'-Dichlorodiethyl Sulfide with Calcium Hypochlorite in Aqueous Solution. Biul. Wojsk. Akad. Tech. 83 (1975). CA 84, 179476u (1976).

93. Edgewood Arsenal DF to Wagner, P. Analysis of HD in Aqueous HTH Solutions (Omnibus Program) 21 July 1973.

94. Redd, R. J. Edgewood Arsenal Letter. Report of Visit to West German Republic 18-22 October 1976. November 1976.

95. Epstein, J. Edgewood Arsenal DF. Heat of Reaction of VX with Alkaline Bleach Solution. 23 May 1973.

96. Wagner, P. Edgewood Arsenal, Demil Progress Report, Omnibus Program 21 October 1976.

97. Wagner, P. Edgewood Arsenal, Demil Progress Report, Omnibus Program 4 February 1977.

98. Fielding, G. H., et al. NRL Report 7067. Disinfection with Hypochlorite. Application to Clothed Men, Construction Materiels, and Electronic and Electrical Items. Naval Research Laboratories, 29 June 1970.

99. Hovanec, J. W., et al. Quarterly Progress Report. Applied Chemistry Section, Chemical Branch, Research Division, CSL, APG. Solubilization of VX and Demilitarization of VX. 11 September 1978.

100. Amos, D. Materials Research Lab, Ascot Vale, Australia. MRL-R-701. Comparison of Fichlor and DS-2 Decontaminants Against Agents HD, GD, and VX and Alkyd and Aliphatic Polyurethane Paints (U). 1974. RESTRICTED Report.

101. Shaw, K. B., and Miller, R. K. Defense Research Establishment, Ottawa. DREO-697. A Laboratory Investigation of Aqueous Formulations of Sodium Dichloroisocyanurate (CDB-63) and Supertropical Bleach (STB) as Chemical Agent Decontaminants (U). June 1974. CONFIDENTIAL Report.

102. J. W. Hovanec, J. A. Albizo, J. R. Ward and L. L. Szafraniec, "A Method for Examining the Degradation of GD and DFP on Reactive Films and Powders" In "Proceedings of the 1987 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research," Rousa, M. D., Ed., CRDEC-SP-00000, 1988, in press.

103. Pitman, I. H., et al. Prediction of Chlorine Potentials of N- Chlorinated Organic Molecules. J. Chem. Soc. Section B. 1230 (1969).

104. Benes, J. Mechanism of the Reaction of Chloramine B with Bis (2-Chloroethyl) Sulfide. Collect. Czech. Chem. Commun. 28, 1171 (1963).

105. Sartori, M. The War Gases p. 232 D. Van Nostrand, New York, New York. 1940.

106. Dismukes, E. B. et al.,Southern Research Institute Contract No. DAAK11-80-C-0036.Evaluation of Decontamination Formulations,Final Report May,1982.

107. Hill, A. E. Compositions for Destruction of Mustard Gas. USPatent 2,926,107. February 23, 1960. CA 54, 13502 (1960).

108. Philipp, C. Rendering B',B'-Dichlorodiethyl Sulfide Innocuous. German Patent 557, 081. June 13, 1928. C. A. 27,355 (1933).

109. Philipp, C. Rendering B',B'-Dichlorodiethyl Sulfide Innocuous. German Patent 590,796. January 9, 1934. C. A. 28, 2433 (1934).

110. Philipp, C. Rendering B',B'-Dichlorodiethyl Sulfide Innocuous. German Patent 588,131. November 12, 1933. C. A. 28, 1427 (1934).

111. Albert, T. J. and Pfansteil, R. Composition for Destruction of Mustard Gas. U. S. Patent 2,927,037. March 1960. C. A. 54, 13503 (1960).

112. Mitchell, T. F., et al. EATR 4781. Decontamination of Chemical Agents on Skin (U). Ocotber 1973. CONFIDENTIAL Report.

113. Gilchrist, M. F. EASP 1300-2. Summary of Study of Decontamination of VX Contaminated Fabrics Using M13 Decontamination Kit. November 1972.

114. Bauer, V. E., et al. CWLR 2231. Chlorination of VX in Dilute Aqueous Solution at 25°C. August 1958.

115. Benson, J. H., et al. EM-TR-73070. Laboratory and Pilot Scale Detoxification of VX in Acidic Media using Chlorine Gas. May 1974.

116. Basset, M. C., et al. EATR-4117. Inproved Fluorescence Method for Analysis of VX in Field Test Samples (U). July 1967. CONFIDENTIAL Report.

117. Sass,S.et al. EC-TR-76120.Identification of Chemical Agents by GLC Employing Retention Indices (U).February 1977.CONFIDENTIAL Report

118. Valis,R.J.,and Vigus,E.S. Nat.Tech.Info.Service Report No.AD-A045475. Pyrolysis of Detoxified Agent Wastes. 2.Drum -Dried Salts From the Acid Chlorinolysis of VX. 1977.

119. Epstein, J., etal. EATM 143-2. Annual Summary of Progress of the Defense Research Development. 1967. April 1969.

120. Preis, S., et al. Melpar, Inc. Contract No. DA18-108-AMC-203(A). Final Report. Study of Chemical Agent Decontamination System for Multipurpose Use. June 1964.

121. Braude, G. L. W. R. Grace, Contract DA-18-035-AMC-287(A). RES-70-41. Research and Feasibility Studies on Clothing and Decontamination. September 1970.

122. A. R. Katritzky, B. L. Duell, H. D. Durst and B. Knier, "Substituted o-Iodoso- and o-Iodoxybenzoic Acids: Synthesis and Catalytic Activity in the Hydrolysis of Active Phosphorus Esters" In "Proceedings of the 1987 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research," Rousa, M. D., Ed., CRDEC-SP-00000, 1988, in press.;

123. H. D. Durst, R. A. Mackay, B. A. Burnside, B. L. Knier and F. R. Longo, "The Hydrolysis of Phosphate Esters in Microemulsions" *ibid.*

124 F. R. Longo, B. A. Burnside, B. L. Knier, H. D. Durst, R. A. Mackay and L. L. Szafraniec "Analysis of the Hydrolysis products of PNDP in Microemulsion Media Via P31-FT NMR" , *ibid.*

125. Mill, T. and Gould, C. W. Stanford Reseach Institute. EC-CR-76050. Contract DAAA15-74-C-0150. Final Report. Oxidation of Sulfur and Amine Model Compounds. January 1976.

126. Bagley, F. D., et al. DPG-TR-A105D. Methodology Study Method for Arriving at Agent Decay Parameters as Cloud Travels Downwind. June 1973.

127. Commerford, G. E., et al. Southwest Research Inst. Contract AF08(635)-5711. Final Report. Air Force Armament Lab. Eglin AF Base. AFTL-TR-67-108. Decontamination with Fire Fighting Equipment. September 1967.

128. Mitchell, T. F., et al. EATR-4781. Decontamination of Chemical Agents on Skin (U). October 1973. CONFIDENTIAL Report.

129. Lindsten, D. C and Des Roches, P. R. Nat. Tech. Info. Service AD Report AD-A046203. Decontamination of Water Containing Chemical and Radiological Warfare Agents by Reverse Osmosis. 1977.

130. Braman, R. S., et al. Garrett Corp. Contract DA18-035-AMC-279. Final Report. CB-67-2378-4.1. Preparation and Evaluation of Non-Carbonaceous Solvents and Collective Protection Against CB Agents. April 1968.

131. Chasanov, G. and Epstein, J. Ion Exchange Resins as Catalysts in the Decomposition of Sarin. J. Polym. Sci. 31, 399 (1958).

132. Janauer,G. E. ARCSL-SP-81023.A Selective Review and Assessment of Potential Applications of Ion-Exchange Resins in Chemical Analysis, Protection and Detoxification.January 1983.

133. Valis, R.J. and Kolakowski, J.E. ARCSL-TR-81092.Development and Application of a Gas Chromatographic Method for Determination of Lewisite Emissions During Incineration of Obsolete Chemical Agent Identification Sets.December 1981.

134. Green,S.J. and Price,T.S. LVI. The Chlorovinylchloroarsines. J. Chem. Soc. 119, 448 (1921).

135. Waters,W.A. and Williams,J.H. Hydrolysis and Derivatives of Some Vesicant Arsenicals. J. Chem. Sos. 18, (1950).

136. Bartlett, P.D. OSRD No.470 Serial No.211. March 31,1942.

137. Buswell, A.M. and Price,C.C. OSRD 4193 June 26,1944.

138. Analytical Division,Research Directorate Analysis of Residual Agent Concentration in Decontamination Solution at the Chemical Transfer Facility APG-EA. Undated.

139. Moynihan, P. I., et al. JPL-D-918-Vol.1-2 Safe Disposal Techniques for DoD Toxic Waste. August 1983.

4.2 Decontamination Protocols - Current

4.2.1. Background - Hazard Evaluation of Decontaminated Liquid Waste at CRDEC

In January 1986 the State of Maryland passed a regulation listing residues of certain decontaminated chemical surety material (CSM) as hazardous waste. Chemical Research, Development and Engineering Center (CRDEC) then initiated a delisting request for these residues, in that they do not meet the criteria for hazardous waste. CRDEC has tasked Research Directorate to provide both analytical and toxicological data that will support this delisting process.

To answer the questions posed to CRDEC by the State of Maryland in their September 1987 letter, the following criteria must be met:

a. CRDEC must provide a detailed description of the actual decontamination procedures used on the laboratory materials. This must include a step-by-step outline of the decontamination process, and must identify the decontamination agent used on a given CSM, the theory of these chemical reaction(s), the concentration of the decontaminating agent used, the amount of time the reaction is allowed to proceed, and note the parameters that influence the degree to which the reaction goes to completion.

b. CRDEC must describe the procedures used to assure that the solutions on which toxicological tests are performed are equivalent to the solutions resulting from the actual decontamination procedures.

c. Finally, CRDEC must describe the protocol for the toxicological testing so that the State of Maryland can determine whether it follows generally accepted practices.

In line with the above questions, this protocol describing in detail preparation of solutions (part b) used by Toxicology Division to verify the decontamination of the CSM in question (Question c above). These were taken from actual decon procedures used at CRDEC. For these tests a decon solution was prepared and divided into two portions. The first portion was analyzed to ensure destruction of agent and analysis of products. The second portion was subjected to toxicological testing. Thus data from these experiments will directly answer the question posed by the State of Maryland as to " procedures used to assure that the solutions on which toxicological tests are performed are equivalent to the solutions resulting from the actual decontamination procedures." The results of this testing schedule is given in Section 4.3.4 below.

The standard decontamination solutions used at CRDEC were chosen for completeness of the decon procedure. The theory of the decon reactions are covered in Sections 2 and 3 and the exact steps involved in making the decon solutions are covered in the General Protocol below. The portion of the solutions used for toxicological testing were adjusted after the decon procedure to ensure good laboratory practice requirements in the toxicological protocol outlined in 4.3.2. Toxicology Division determined by oral and inhalation route in rats, and by the dermal route in rabbits, that tested CSM were detoxified to a level less than a Class "B" poison using currently approved test procedures as spelled out in CFR 49 Department of Transportation (DOT) tests. The toxicity criteria for a class "B" poison are the same as the State of Maryland's criteria for hazardous waste.

4.2.2. Hypothesis.

Chemical decontamination of CSM, followed by neutralization and subsequent oral, dermal and inhalation toxicity tests, will show that the original

CSM have been decontaminated/deactivated in line with the State's letter to require that "residues no longer contain materials for which it was listed.

4.2.3. Approach.

The following agent/decon systems are routinely used for decontamination of listed agents in research quantities. Nmr evidence is given in Appendix as to the extent of reaction. Note in all cases that the nmr technique is accurate only to 99.5% destruction. Other analytical procedures must be utilized for more accurate quantitation.

	Agent	Recomended Decon Solution
1.	GA, GB, GD, L	10% NaOH
2.	GA, GB, GD, L	10% Na_2CO_3
3.	GA, GB, GD,	10% Alcoholic NaOH
4.	VX	10% $Ca(OCl)_2$ (HTH) plus 10% alcoholic NaOH
5.	GA, GB, GD, VX	10% $Ca(OCl)_2$ (HTH)
6.	GA, GB, GD, HD, L	5.25% NaOCl
7.	HD	Concentrated HNO_3
8.	GB	Monoethanolamine, Neat and 25% aqueous

Agent/Decon systems are selected on the basis of wide use in Research Directorate and Research, Development, & Engineering Support Division. Of the nerve agents, VX is the most difficult to decon by virtue of its reduced reactivity and solubility relative to the G agents; thus, both a VX/10% $Ca(OCl)_2$ (HTH) plus 10% alcoholic NaOH (standard solution 4 above) and a VX/10% $Ca(OCl)_2$ (HTH) (standard solution 5 above) system are reported. The decon of GB and GD are similar with the exception that GB it is more soluble and hydrolyzes more rapidly then GD. Extensive toxicological data for GB already exists. In order to minimize precipitation during HD decontamination in research quantities, NaOCl is used as the source of chlorine instead of $Ca(OCl)_2$.

4.2.4. Step-by-Step Outline of the Decontamination Process. The following are examples of the general protocol for listed compounds as decontaminated using accepted protocols at CRDEC.

4.2.4.1. Materials

4.2.4.1.1 10% NaOH Solution: A stock 10wt % NaOH/water solution will be prepared using distilled water and dry sodium hydroxide pellets of flakes in a ratio of 100g NaOH to 900g water. NaOH should appear dry and not stick together. The mixture should be stirred until all NaOH has dissolved.

4.2.4.1.2 10% Alcoholic NaOH Solution: 100 mL of denatured ethyl alcohol (95%) is added to each 900 mL of the NaOH solution described in paragraph 4.1.4.1.1.

4.2.4.1.3 10% Na_2CO_3 Solution: A stock 10wt % Na_2CO_3/water solution will be prepared using distilled water and dry sodium carbonate powder in a ratio of 100g Na_2CO_3 to 900g water. The Na_2CO_3 should appear dry and not stick together. The mixture should be stirred until all Na_2CO_3 has dissolved.

4.2.4.1.4 10% HTH Solution: A stock 10 wt % $Ca(OCl)_2$/water solution will be prepared using tap water in a ratio of 100g HTH to 900g water. The HTH should appear dry and not stick together. The mixture should be stirred until all the HTH has dissolved. Dry HTH typically contains 55% $Ca(OCl)_2$. Appropriate additions of dry HTH must be made if the HTH contains less than 55% $Ca(OCl)_2$. The amount of dry HTH may be computed by:

[55/percent purity of $Ca(OCl)_2$] X 100g = g of HTH in 900 mL water

In no instance will dry HTH with less than 30% $Ca(OCl)_2$ will be used.

4.2.4.1.5 Alcoholic HTH Solution: 100 mL of denatured ethyl alcohol (95%) is added to each 900 mL of the HTH solution described in paragraph 4.2.4.1.4.

4.2.4.1.6 5.25% NaOCl Solution: Commercial grade 5.25% strength aqueous NaOCl is used. The material must be certified, by analysis, to contain > 4.00% active chlorine before use.

4.2.4.1.7 Concentrated HNO_3 Solution: Commercial concentrated (65-70%) aqueous nitric acid is used undiluted.

4.2.4.1.8 Monoethanolamine, Neat: Material from supplier (> 95%, such as Aldrich) will be use directly without dilution with water.

4.2.4.1.9 25% Monoethanolamine Solution: A stock 25wt % MEA/water solution will be prepared using distilled water and neat liquid MEA in a ratio of 250g MEA to 750g water. The mixture should be stirred until all MEA has dissolved.

4.2.4.2. GENERAL INSTRUCTIONS FOR DECONTAMINATION

4.2.4.2.1 Decon procedures will be conducted at an ambient temperature between 20 and 26°C. Solutions will be allowed to come to ambient temperature before initiation of the decontamination protocol. Temperature will be recorded.

4.2.4.2.2 Agitation of agent/decontaminant mixture must be maintained for a minimum of one hour.

4.2.4.2.3 Agent must be added to the decontaminant (NOT DECONTAMINANT TO THE AGENT).

4.2.4.2.4 Reaction vessel must be large enough and open enough to withstand substantial exothermic reactions.

4.2.4.2.5 The concentrations of NaOH, Na_2CO_3 or $Ca(OCl)_2$ solutions represent the minimum to be used.

4.2.4.3. PROTOCOL FOR DECONTAMINATION OF GA

4.2.4.3.1 GA is decontaminated with the 10% NaOH solution (4.2.4.1.1). GA is soluble at 7 parts GA per 100 parts water.

4.2.4.3.2 A minimum of 55 grams of decon solution is required for each gram of GA. This ratio ensures that there is at least 22 moles of base for each mole of GA.

4.2.4.3.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour followed by reaction period of 23 hours with total decontamination assured after the solution has reacted for 24 hours. Agitation is not necessary following the first hour of the entire 24 hours.

4.2.4.3.4 At the end of 24 hours, the resulting solution should be titrated to a pH between 10 and 12.

4.2.4.3.5. After completion of the 24 hour reaction period, the decontamination solution must be treated with excess 5.25% NaOCl solution (4.2.4.1.7, commercial bleach, at least 2.5 mole OCl^- /mole GA) to destroy the CN^- formed during hydrolysis. For example, 20 g of GA is reacted with 1100 g 10% NaOH solution, then reacted with 600g 5.25% NaOCl (stoichiometric amount at 2.5 mole OCl^- /mole GA = 525g of 5.25% NaOCl). This solution is allowed to react for two hours to ensure destruction of cyanide. Before transfer to sump test for presence of active chlorine by use of acidic potassium iodide solution give free iodine color. If negative, add additional 5.25% NaOCl solution, wait for two hours, then test again for active chlorine. Continue procedure until positive chlorine is given by solution.

4.2.4.3.6. Alternate solutions for the decontamination of GA. It is permitted to substitute 10% Na_2CO_3 (4.2.4.1.3) for the 10% NaOH solution above. Continue with same ratios and the same time stipulations.

4.2.4.4. PROTOCOL FOR DECONTAMINATION OF GB

4.2.4.4.1 GB is decontaminated with the 10% NaOH solution (4.2.4.1.1). GB is miscible with water.

4.2.4.4.2 A minimum of 55 grams of decon solution is required for each gram of GB. This ratio ensures that there is at least 22 moles of base for each mole of GB.

4.2.4.4.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour. Agitation is not necessary following the first hour.

4.2.4.4.4 At the end of one hour, the resulting solution should be titrated to a pH greater than 11.5.

4.2.4.4.5. Alternate solutions for the decontamination of GB. It is permitted to substitute 10% Na_2CO_3 (4.2.4.1.3) for the 10% NaOH solution above. Continue with same ratios but increase the time of reaction from one to three (3) hours.

4.2.4.4.6 Alternate solutions for the decontamination of GB. It is permitted to substitute 5.25% NaOCl (4.2.4.1.6) for the 10% NaOH solution above. Continue with same ratios and the same time stipulations.

4.2.4.4.7 Alternate solutions for the decontamination of GB. It is permitted to substitute 25% MEA (4.2.4.1.9) for the 10% NaOH solution above. Continue with same ratios and the same time stipulations.

4.2.4.5. PROTOCOL FOR DECONTAMINATION OF GD

4.2.4.5.1 ~~GB~~ GD is decontaminated with the 10% NaOH solution (4.2.4.1.1). GD is miscible with water.

4.2.4.5.2 A minimum of 55 grams of decon solution is required for each gram of GD. This ratio ensures that there is at least 22 moles of base for each mole of GD.

4.2.4.5.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour. Agitation is not necessary following the first hour.

4.2.4.5.4 At the end of one hour, the resulting solution should be titrated to a pH greater than 11.5.

4.2.4.5.5. Alternate solutions for the decontamination of GD. It is permitted to substitute 10% Na_2CO_3 (4.2.4.1.3) for the 10% NaOH solution above. Continue with same ratios but increase the time of reaction from one to three (3) hours.

4.2.4.5.6 Alternate solutions for the decontamination of GD. It is permitted to substitute 5.25% NaOCl (4.2.4.1.6) for the 10% NaOH solution above. Continue with same ratios and the same time stipulations.

4.2.4.6. PROTOCOL FOR DECONTAMINATION OF VX

4.2.4.6.1 Procedure for decontaminating up to 50g of VX.

4.2.4.6.1.1 VX is decontaminated with the 10% HTH solution (4.2.4.1.4).

4.2.4.6.1.2 The minimum decontaminating solution to agent ratio is 8.25 moles of Ca(OCl)2 for each mole of VX. For the 10% HTH solution, 80 grams of decon solution is required for each gram of VX.

4.2.4.6.1.3 Solution is agitated or stirred for a minimum of one hour. If phasing of agent/decontaminant persists after 5 minutes, an amount of denatured ethyl alcohol equal to 10% (weight) of the total agent/decontaminant solution may be added to assist miscibility.

4.2.4.6.1.4 Upon completion of a minimum one hour agitation, the resulting solution is titrated to a pH between 10 and 12.

4.2.4.6.2 Decontamination of VX in excess of 50 grams.

4.2.4.6.2.1 A 10% alcohol HTH solution (4.2.4.1.5) is used to decontaminate 50g or more of VX.

4.2.4.6.2.2 Fourteen grams of alcoholic HTH solution is used for each gram of VX.

4.2.4.6.2.3 Solution is allowed to agitate for a minimum of one hour.

4.2.4.6.2.4 Upon completion of a minimum of one hour agitation, 10% NaOH solution is added to the resulting solution in a quantity equal to that necessary to assure that a pH of 12.5 is maintained for a period of not less than 24 hours.

4.2.4.7. PROTOCOL FOR DECONTAMINATION OF L (LEWISITE)

4.2.4.7.1 L is decontaminated with the 10% Alcoholic NaOH solution (4.2.4.1.2). L is poorly soluble in water.

4.2.4.7.2 A minimum of 200 g of decon solution is required for each gram of L. This ratio ensures that there is at least 78 moles of base for each mole of L.

4.2.4.7.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour. Agitation is not necessary following the first hour.

4.2.4.7.4 At the end of one hour, the resulting solution should be titrated to a pH greater than 11.5.

4.2.4.7.5. Alternate solutions for the decontamination of L. It is permitted to substitute 10% alcoholic Na_2CO_3 (solution 4.2.4.1.3 made up with 10% alcohol) for the 10% alcoholic NaOH solution above. Continue with same ratios but increase the time of reaction from one to three (3) hours.

4.2.4.7.6 Alternate solutions for the decontamination of L. It is permitted to substitute 5.25% NaOCl (4.2.4.1.6) for the 10% alcoholic NaOH solution above. Continue with same ratios and the same time stipulations.

4.2.4.8. PROTOCOL FOR DECONTAMINATION OF HD

4.2.4.8.1 HD is decontaminated with the 5.25% NaOCl solution (4.2.4.1.6). HD is poorly soluble in water.

4.2.4.8.2 A minimum of 65 grams of decon solution is required for each gram of HD.

4.2.4.8.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour. Agitation is not necessary following the first hour.

4.2.4.8.4 At the end of 24 hours, the resulting solution should be titrated to a pH between 10 and 12. Test for presence of active chlorine by use of acidic potassium iodide solution give free iodine color. If negative, add additional 5.25% NaOCl solution, wait for two hours, then test again for active chlorine. Continue procedure until positive chlorine is given by solution.

4.2.4.8.6. Alternate solutions for the decontamination of HD.

4.2.4.8.6.1. HD is decontaminated with the 10% $Ca(OCl)_2$ solution (4.2.4.1.4). HD is poorly soluble in water.

4.2.4.8.6.2 A minimum of 65 grams of decon solution is required for each gram of HD.

4.2.4.8.6.3 Decontaminant/agent solution is allowed to agitate for a minimum of one hour. Agitation is not necessary following the first hour.

4.2.4.8.6.4 At the end of 24 hours, the resulting solution should be titrated to a pH between 10 and 12. Test for presence of active chlorine by use of acidic potassium iodide solution give free iodine color. If negative, add additional 10% $Ca(OCl)_2$ solution, wait for two hours, then test again for active chlorine. Continue procedure until positive chlorine is given by solution.

4.2.5. Analysis.

NMR analysis is performed to characterize the products formed, however the techniques are not sensitive enough to determine trace amounts of agents (< 0.5%).

4.2.5.1 ^{31}P NMR.

The GA, GD, and two VX decon products will be analyzed by ^{31}P NMR. Samples will consist of 0.5 to 1 mL in 5 mm NMR tubes. Spectra will be recorded on a Varian XL-200 Superconducting FT-NMR System operating at 81 MHz in an unlocked mode. Spectra will be obtained at probe temperature (ca. 21°C), using phosphoric acid (85%) as the external reference. The chemical shift values (δ) determined are good to better then - 0.1 ppm. Data will be accumulated from 2 to 18 hours depending on signal-to-noise levels. All

spectra will be obtained using a pulse width of 3 µsec (33 degree), a sweep width of 20 KHz, an acquisition time of 1.6 sec, and a pulse delay of 2.5-3.3 sec. Grated decoupling will be used to eliminate any nuclear Overhauser effects, and quantitative data will be obtained by digital integration of the peak areas. Detectable limit: 200µg of agent/mL of original decon solution.

4.2.5.2 ^{13}C NMR.

The HD decon product will be analyzed by ^{13}C NMR. Samples will consist of 0.5 to 1.0 mL in 5 mm NMR tubes. Spectra will be recorded on a Varian XL-200 Superconducting FTNMR System operating at 50 MHz in an unlocked mode. Spectra will be obtained at probe temperature (ca. 21°C), using tetramethylsilane (TMS) in chloroform as the external reference. The chemical shift values (δ) determined are good to better then -0.1 ppm. Data will be accumulated from 2 to 18 hours depending on signal-to-noise levels. All spectra will be obtained using a pulse width of 3.5 µsec (33°), a sweep width of 12 KHz, an acquistion time of 1.6 sec, and a pulse delay of 2.5-3.0 sec. WALTZ decoupling will be used for full proton decoupling, and quantitative data will be obtained by digital integration of the peak areas. Detectable limit: 0.5-1mg of agent/mL of original decon solution.

4.2.5.3 Potassium iodide test for active chlorine.

Place roughly 3 mL decon solution in a small erlenmeyer flask. Add several crystals of potassium iodide and swirl to dissolve. Using a small graduated cylinder rapidly add about 3 mL of a 50 wt.% sulfuric acid/water and swirl. An immediate iodine red color shows the presence of active chlorine. (NOTE: A gradual appearance of red indicates air oxidation of the potassium iodide and not chlorine. To be considered positive the red color must appear immediately upon addition of the acid mixture.)

4.2.6. Data Storage

Test data will be recorded in official CRDEC notebooks.

The data recorded will include:

a. Complete record of chemical substances used to include lot number and manufacturer.

b. Starting purity of the chemical agents.

c. Quantities of chemicals and agents used.

d. Time allowed between adding agent and neutralizing decon.

e. pH after decontamination step and after neutralization step.

f. Analysis of products.

g. Record laboratory temperatures during decon step.

i. Any problems that arise and how problem was solved.

j. Any changes necessary to the procedures spelled out in this protocol will be documented.

4.3 Toxicology Protocols - Current

4.3.1 INTRODUCTION

The Good Laboratory Practices (GLPs) were the first significant regulations implemented without a preceding catastrophe that had impacted on the health and safety of the American public. Although considerable data were falsified and misrepresented prior to the implementation of the GLPs, there is no documentation that products registered or approved using the faulty data, caused any significant harm to the public.

The first Pure Food and Drug Law passed in 1906 resulted from the contamination and filth exposed in the meat packing industry (see Upton Sinclair, The Jungle), foods adulterated with chemical preservatives (Dr. Harvey Wiley's Poison Squad), and quack remedies. This law, also known as the Wiley Act, prohibited the manufacture and interstate shipment of adulterated and misbranded foods and drugs.

In 1938 the Federal Food, Drug, and Cosmetic Act (FFDCA) was passed, prompted in part from the Elixir Sulfanilamide episode in 1937 that had resulted in over 100 deaths. Although sulfanilamide tablets and powder had previously been used safely and effectively for the treatment of streptococcal infections, the elixir, in diethylene glycol (antifreeze) had not been tested for toxicity, nor was it a requirement by law at that time. The 1938 FFDCA required that drug manufacturers provide scientific proof that new products were safe for use before they could be marketed.

Following the thalidomide tragedy in Europe, where thousands of deformed infants were born to mothers who had taken this new drug, the 1962 Kefauver-Harris amendment was passed. This served to strengthen the FFDCA by requiring that not only safety had to be demonstrated for any new drug, but also efficacy. Additionally, adverse reactions were to be reported, advertising had to be accurate and complete, and Good Manufacturing Practices Regulations (GMPs) were established. The GMPs set standards for plant facilities, their maintenance, and laboratory controls in an attempt to prevent errors or accidents that could harm consumers.

Compliance with GLPs, although cumbersome to implement and considered a nuisance and waste of time by some study directors or principal

investigators, can really be advantageous in the management and validation leading to the acceptance of the study by regulatory agencies and peers.

The GLPs are here to stay and most laboratories have or are implementing them. The key to their successful implementation and execution is to participate, document, and validate. The most recent GLPs of December 28, 1987 are in Appendix 8.2.1.

4.3.2 TOXICOLOGY DIVISION GLP COMPLIANCE MEASURES

The management of Toxicology Division established a Quality Assurance Unit to implement Good Laboratory Practice standards in all studies performed by the division. QAU personnel consists of two individuals who are responsible for many tasks relating to each study. The GLP standards impact many areas including : management's responsibility, maintenance of the physical plant, (especially animal care and laboratory facilities), personnel, equipment maintenance and calibration, SOP's , test and control substances characterization, handling and storage, the study protocol and conduct, and reporting and record retention.

The specific tasks assigned to the Quality Assurance Unit are detailed below. The protocol for the study is reviewed by the QAU to assure that the study director has suitably addressed the study parameters listed in the act. All protocols are maintained in the office of the QAU while studies are in progress. Copies of Standard Operating Procedures (SOP) for laboratory and facility operations are reviewed when prepared and maintained by the QAU. A Master Schedule is maintained which lists and details pertinent information for each study. The schedule is periodically updated and treated as raw data. All studies are subject to inspection of critical phases by the QAU. The inspections are beneficial in identifying problems and recommending actions to resolve them. They also serve as a mechanism to notify management when problems exist which may affect the integrity of the study. The QAU is tasked with determining that no deviations from approved protocols and/or SOP's were made without proper documentation. The final report of the study is reviewed by the unit to assure that the report describes the methods used to generate data and that the results reported accurately reflect the raw data. The standards require the QAU to prepare a statement for inclusion in the final report which documents when inspections were made and the findings of the same reported to management and the study director. An archive for retention of raw data and documents required to validate the study is maintained by the QAU. The statute mandates retention of records for at least ten years following conclusion of the study.

4.3.3 ARCHIVE RECORDS

CRDEC has reviewed the toxicology data base of unpublished data going back to the early 1960's to determine its applicability to address the current issues.

The data collected and presented in summary form are found in Appendix 8.2.2. This table indicates that the lethal dose 50 (LD_{50}) of the test samples are greater than those considered hazardous waste. This indicates that decontaminated solutions tested were less toxic than the COMAR criteria 10.51.02.08. The methods used to generate the toxicity data in our laboratories follow the guidelines as described by the Department of Transportation (DOT), the Food and Drug Administration (FDA) Federal Hazardous Substance Act (FHSH). For the current tests, the protocols utilized at CRDEC are contained in the Appendix and conform to the Department of Transportation requirement for class "B" poison, also defined in Appendix 8.2.4. The detailed chemical reactions of the current standard operating procedure for decontamination/detoxification are described in the Sections 4.1 and 4.2 above.

Decontamination procedures for lethal chemical warfare agents have been fully developed by the research staff of CRDEC. A comprehensive literature survey is presented in Sec. 4.1. This survey covers the experimental decontamination procedures examined in the laboratories for the destruction of chemical agents. Edgewood Arsenal Technical Report EATR-4755 (Owens, et al, 1973) utilized some of the experimental methods described in the literature survey on deconned agent samples provided by the Chemical Process Laboratory and the resulting toxicities were determined.

Lewisite, an arsenical vesicant produced for World War II, subjected to basic solutions decomposes to the inorganic arsenite, chloride and acetylene. The chemical literature of the early 1940's reported these studies in detail, Waters and Willians (1950). The chemical literature of the organometallic arsenic compounds of Lewisite has been reviewed by Doak and Freedman (Organometallic Compounds of Arsenic, Antimony and Bismuth, John Wiley & Sons, Inc., New York, 1970, p. 65, 89- 90, 103-104, 109-110).

In practice, to assure fast and complete destruction of the toxic agents, a large excess of the decontaminant is used, so that, the agent is always present in concentrations that would assure the reactions would proceed with rates similar to, if not the same as, the first order reaction rates. Before the wastes are disposed of they are checked to insure that active decontaminant remains in the spent solutions. These waste are then transferred by a number of mechanisms (i.e. transfer in steel drums or by closed waste drain lines) to a waste collections system for ultimate disposal. We have found no record of adamsite (K996) use or decontamination, however, incineration appears to be the detoxification method of choice. There was also no toxicological data found for decontaminated GD (K993). However, its chemistry is well defined and detoxification is accomplished by hydrolysis.

Decontaminated GA (K991) (Appendix 8.2.2) indicates that the LD_{50} is less than 50 mg/kg by the oral route suggesting it is a hazardous substance orally, but not dermally. Our records show that GA in this experiment was detoxified to produce sodium cyanide which could account for the oral toxicity. The standard procedure now used at CRDEC provides for destruction of the cyanide by oxidation with sodium hypochlorite subsequent to hydrolysis.

Agent T (K998) is a mustard and was not used as a separate filling in munition. However, agent T is found as a mixture/solution with HD and is listed as HT. Therefore, separate agent T (K998) is not applicable and should be delisted.

4.3.4 RESULTS OF CURRENT TESTS

Recently CRDEC identified three decon solutions for further testing. These were VX/10% $Ca(OCl)_2$, GD/10% NaOH, and HD/5.25% NaOCl and were tested in rabbits dermally and in rats by the oral and inhalation routes according to the protocols in the Appendix. These 48 hour DOT tests require that if 4 or fewer of a group of 10 animals (5 of each sex) die during the test, the test is negative. That is, it is less than a class B poison. If 5 or more die, the material would be listed as a class B poison, and thus a hazardous waste.

The dose levels used were 0.2 mL/kg dermally in rabbits, 0.05 mL/kg orally in rats, and a target concentration of 2 mg/kg by inhalation in rats.

Results: None of the animals died in these tests. The results are presented in the following table.

Materials and 48 Hour Mortality

Species (route)	Dose mL/kg	$VX/Ca(OCl)_2$ # Dead/#Tested	GD/NaOH # Dead/#Tested	HD/NaOCl # Dead/#Tested
rabbit[1] (dermal)	0.2	0/10[a]	0/10	0/10[b]
rat[1] (oral)	0.05	0/10	0/10	0/10
rat[2] (inhal)	10mg/L (M)	0/5[c]		
	10mg/L (F)	0/5[c]		
	6mg/L (M)		0/5	
	7mg/L (F)		0/5	
	13mg/L			0/5[c]
	18mg/L			0/5[c]

[a] Mild skin irritation observed in 4 of 10 rabbits prior to 24 hours with $VX/Ca(OCl)_2$ which disappeared by 48 hours.

[b] Mild skin irritation observed in 10 of 10 rabbits after 24 hours with HD/NaOCl and persisted for 48 hours.

[c] During exposure to $VX/Ca(OCl)_2$ and HD/5.25% NaOCl the rats appeared to be lethargic and showed signs of mucous membrane irritation. These effects were present only during the exposure.

[1] Notebook reference 88-0005, pages 4-13.

[2] Notebook reference 87-0128, pages 18-33.

Note: Although no deaths occurred in any of the tests conducted, the concentrations generated for the inhalation exposures far exceeded the target of 2 mg/L and may in part explain the observations reported.

BLANK PAGE

5.0 ANALYTICAL METHODS

5.1 Introduction

Decontamination studies generally are conducted to determine the rate of reaction of a chemical warfare agent with a known decontaminant in a well defined media. These studies require that the systems under investigation be amenable to analysis of either the starting materials or their reaction byproducts. In most cases the rate of disappearance of the chemical agent was selected since oxidation reactions in general are difficult to study by examining the reaction byproducts. The analytical methods employed were calibrated for the systems and would not as a general rule be methods of analysis for a broad spectrum of conditions. Methods such as Ultraviolet adsorption spectrometry were commonly used, since the chemical agents have an absorption and the reaction products do not. These techniques were especially useful is studying the very fast reactions indicative of the G-Agents with strong basic solutions. When the Chemical Demilitarization Project Officer (Demil PO) was established in the late 1960's, these methods of analysis used for decontamination studies were not acceptable to the regulatory agencies established to oversee and approve these disposal operations. As a result CRDEC in concert with the Demil PO, investigated a number of alternate methods of analysis suitable for these operations. Due to the uniformity of demil operations, the analytical methods used, to control and validate these disposal process, could be tailored and made specific for the disposal process. The methods reviewed in this presentation cover classical visible/ultraviolet, fluorescence and enzymatic colorimetry, chromatography including thin layer, high performance liquid, and gas/liquid, in addition to specialized methods used in the demilitarization operations. No review of analytical methodology would be complete without adequate discussion of the sampling and clean-up procedures, and some assessment of the quality of the results based on established standards and good laboratory practices.

5.2 Chromatographic Analysis

5.2.1 Gas/Liquid Chromatography (GLC):

A review of analytical procedures for GB and VX by Crabtree and Sarver[5-1] provides an acceptable discussion of using this instrumental methods of analysis. There has been little change in the instrumentation since this review. Several unique arrangements of specific detectors have improved there sensitivity; however, these improvements are not measured in orders of magnitude, but within the same order. Packed column technology was used routinely at time of the review and not references to capillary wall coated open tube (WCOT) colums were available at that time. This advancement has been incorporated into most of the methods used in the demil operations. Southern Research under contract to U.S. Army Toxic and Hazardous Materials Agency (THAMA) developed a series of methods for analyzing the chemical warfare agents GB, VX, and HD[5-2].

5.2.2 Sampling and Clean-up Techniques for GLC:

Detection and quantification of the Chemical Warfare Agents GB, VX, HD, and L in strong solutions, used for laboratory decontamination, where the agent is always presence in vanishingly small quantities presents unique sampling problems. In order to demonstrate the effectiveness of the sampling procedure and ultimately the decontamination process, a modified quench process is used. This process requires neutralization of the decontaminant followed by extraction of the neutralized solution with an agent laden extraction solvent. If the agent is then recovered and quantified, the analytical method is considered to be adequate to determine residual agent in the neutralized decontaminant. In the case of GB, salt has to be added to the neutralized decontaminant to saturation so that the extraction efficiency (64%)[5-2c] is favorable to the organic solvent. Procedures for doing this type analysis for GB, VX, and HD are given by Smith and Fowler[5-2]. In the late 1970's, Southern Research under contract to THAMA developed a sries of air monitoring systems based on the use of solid sorbent bed sampler, the Automatic Chemical Agent Air Monitoring System (ACAMS).[5-3b] This effort along with those under the CRDEC Depot Area Air Monitoring System (DAAMS) program have lead to the development of highly sensitive and specific methods of analysis for the CW agents, HD, GB, and VX. Employment of these methods require the modification of the Injection Port of commercially available GLC's. Once this has been accomplished the extract is loaded on the sorbent bed by aspiration from a glass wool plug containing the agent laden extract. The plug is removed, and the glass tube containing the sorbent bed is thermal blackflushed by the GC carrier gas onto the analytical GLC column. For the listed CW agent HD, GB, and VX, the gas chromatograph is equipped with a Flame Photometric Detector (FPD). These methods work well in the low to medium ultra-trace (PPB) levels. At present no equivalent method of analysis is available for Lewisite, however, several excellent projects carried out by S. F. Hallowell and P. C. Bossle have resulted in numerous approaches using both GLC and other types of chromatography and instrumentation that could ultimately lead to a specific and sensitive method of analysis[5-6].

5.2.3 Other Chromatography Methods:

5.2.3.1 Thin Layer Chromatography. Crabtree and Sarver[5-1] contains a good review of this method. Due to the inherent lack of good sensitivity of this method, no further discussion is appropriate.

5.2.3.2 High Performance Liquid Chromatography Methods. Bossle[5-7, 5-8 and 5-9] has developed a direct method of analysis for Mustard, HD, and Lewisite, L, and hydrolysates in aqueous solutions which is effective in low PPM's to the high PPB's. These methods are based on reverse phase chromatography using spectrophotometric and electrochemical detection.

5.3 References

5-1. Crabtree, E. V., Sarver, E. W. EC-TR-76021. Review of Analytical Procedures for GB, VX, and Their Degradation Products. Jan 1977 (U).

5-2. Smith, J. E., Jr., and Fowler, W. K. Analytical Methods Development - Volume 2 - Standing Operating Procedures. Contract DAAK11-82-C-0162 Final Report. Dec 1985 (U); b. Benson, J. H., etal. EM-TR-73070. Laboratory and Pilot Scale Detoxification of VX in Acidic Media Using Chlorine Gas, May 1974.; c. Mohrman, G. B., Rocky Mountain Arsenal SOP NO: SARRM-TOE-17. Index for Low Level Sarin (GB). MAR, 1979.

5-3. a. Duggan, M. L. ARCSL-TR-78048. Pilot-Scale Incineration and Detection Interference Studies for the Disposal of Toxic Gas and War Gas Identification Set; b. Sides, Gary D., Contract DAAK11-77-C-0075. Construction, Development, and Testing of an Automatic Continuous Air Monitoring System (ACAMS) for Use at the Chemical Agent Munitions Disposal System (CAMDS), Dec 1984.

5-4. Soderquist, C. J., Crosby, D. G., and Bower, J. B. Determination of Cacodylic Acid (Hydroxydimethylarsine Oxide) by Gas Chromatography. Anal. Chem. 46, 155-157, (1974).

5-5. Sarver, E. W. Unpublished Results (1974).

5-6. Hallowell, S. F., and Bossle, P. C. Personal Communication and Unpublished Results (1980-1986).

5-7. Bossle, P. C., Martin, J. J., and Sarver, E. W. High Performance Liquid Chromatography Analysis of 2-Chloroethyl Ethylsulfide and its Decomposition By-Products by Derivatization. J. Chromatog. 263, 412-416 (1984).

5-8. Bossle, P. C., Hallowell, S. F., Reutter, D. J., and Sarver, E. W. The analysis of 2,2'-Thioethanol, a Water Soluble Alkyl Sulfide in Aqueous Matrices by LCEC. J. Chromatog. 330, 388-391 (1985).

5-9 Bossle, P. C. Determination of Lewisite Contamination in Environmental Waters by HPLC. Rocky Mountain Analytical Conference, 31 JUL - 5 AUG 1988, Denver, CO.

BLANK PAGE

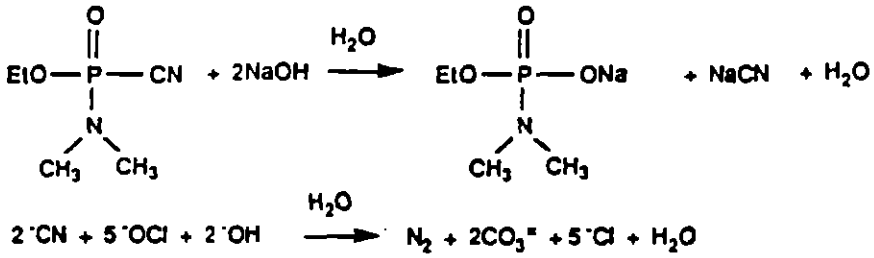
6 Summary of Data

Introduction

In practice, to assure fast and complete destruction of the toxic agent(s), a large excess of the decontaminant is always used; thus the agent is always present in concentrations that would assure the reactions would proceed with rates similar to, if not the same as, the first order reaction rates.

6.1 Ethyl dimethylamidocyanophosphate (GA, Tabun)

GA is routinely decontaminated with 10% sodium hydroxide solution (see Section 4.2). This reaction is extremely fast (estimated half-life < 5 sec) and rapidly releases cyanide. The second step in the decon procedure is the well known reaction of cyanide with hypochlorite (Kirk-Othmer Encyclopedia of Chemical Technology. 3d Edition. Vol. 7 John Wiley and Sons, New York, New York, 1979, pages 316-7) to form nitrogen gas. Thus the overall decon reaction takes place in two steps according to the following reaction:

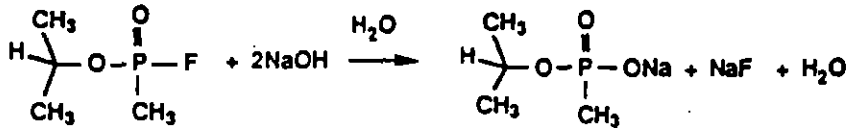


GA is also rapidly deconned (10 half-lives of destruction in 30 minutes or less) using sodium carbonate solutions, aqueous solutions of hypochlorite, and alcoholic sodium hydroxide (see Appendix 8.1.9-8.1.12. Please note that the nmr experiment as presented is designed to show the products of phosphorous hydrolysis. Although routine procedure is to treat the solution with hypochlorite following hydrolysis in the second step, this nmr experiment is not designed to observe cyanide. Thus the equation showing the stoichiometry of the reaction in 8.1.9-8.1.12 is representative only of the first step, the procedure where the measurement is valid. The decontamination is also quite rapid when calcium

hypochlorite is used in conjunction with organic emulsions (the German C8 emulsion). Toxicological tests (see Appendix) of GA detoxified waste show Oral LD_{50} values < 50 mg/kg (Rat, probably due to presence of cyanide in the solution tested) and Dermal LD_{50} values of > 200 mg/kg (Rabbit). The present procedure at CRDEC is to treat the decon solution, following hydrolysis, with hypochlorite to destroy the cyanide.

6.2 Isopropyl methylfluorophosphonate (GB, Sarin)

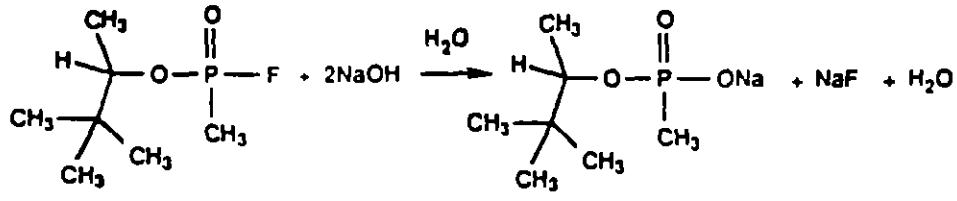
Extensive data exists on the decontamination of GB. This reaction is extremely fast (estimated half-life < 5 sec) and rapidly releases fluoride according to the following reaction:



GB is routinely decontaminated using 10% sodium hydroxide, 10% sodium carbonate, 5.25% sodium hypochlorite, neat monoethanolamine, and by a 25% aqueous monoethanolamine. The decontamination is also quite rapid when calcium hypochlorite is used in conjunction with organic emulsions (the German C8 emulsion). Toxicological tests (see Appendix) of GB detoxified waste show Oral LD_{50} values > 50 mg/kg (Rat) and Dermal LD_{50} values of > 200 mg/kg (Rabbit). Because of the extensive work in the Demil program with GB, additional tests show Oral LD_{50} values 566 mg/kg (Rat- 24 hr), 271 mg/kg (Rat- 14 day) and Dermal LD_{50} values of > 200 mg/kg (Rabbit). In all cases nmr analysis of product formation (see Appendix) confirmed earlier work showing the speed of decontamination (10 half-lives < 5 minutes).

6.3 Pinacolyl methylfluorophosphonate (GD, Soman)

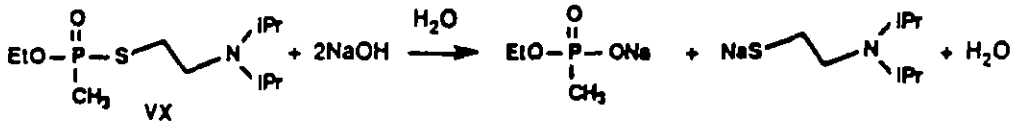
The chemistry of GD is very similar to that of GB, both in reaction kinetics and product formation. The product phosphonic acid differs from the GB products only in the alcohol portion (pinacoyl rather than isopropyl) according to the following reaction:



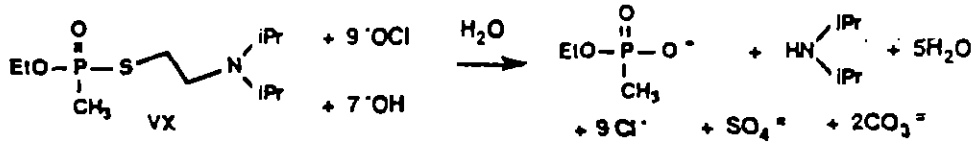
GD is routinely decontaminated using 10% sodium hydroxide, 10% sodium carbonate, 5.25% sodium hypochlorite, neat monoethanolamine, and by a 25% aqueous monoethanolamine. The decontamination is also quite rapid when calcium hypochlorite is used in conjunction with organic emulsions (the German C8 emulsion). There was no extensive toxicological data found for decontaminated GD (K993). However, its chemistry is well defined when detoxification is accomplished by hydrolysis. Toxicological tests (see Appendix) of aqueous hydroxide GD detoxified waste show Oral LD_{50} values > 50 mg/kg (Rat) and Dermal LD_{50} values of > 200 mg/kg (Rabbit). In all cases nmr analysis of product formation (see Appendix) confirmed earlier work showing the speed of decontamination (10 half-lives < 5 minutes).

6.4 O-Ethyl-S-(2-diisopropylaminoethyl) methylphosphonothioate (VX)

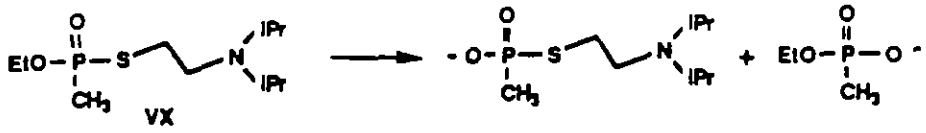
VX is more resistant to cleavage by bases than GA, GB, and GD and treatment with strong base (hydroxide) and/or hypochlorite for longer reaction periods is the recommended procedure. This reaction is moderate (estimated half-life < 900 sec) and releases the thio fragment in a similar mechanism to that observed for GA, GB, and GD, as shown below:



One major concern with VX is its reduced solubility in aqueous solutions, thus alcoholic co-solvents are recommended during the decontamination reaction of quantities greater than 50g. Treatment of dilute VX with aqueous hypochlorite reacts at phosphorous to give ethyl methylphosphonic acid, shown in the reaction below:



In the reaction of VX with alcoholic 10% sodium hydroxide the hydrolysis is similar to hydrolysis using hypochlorite. In extensive studies related to large scale Demil procedures, treatment of VX produces the biproduct from the "bis' impurity to yield waste which is initially tested as toxic by intravenous injection, weakly toxic by oral administration, but exhibits no dermal toxicity. The biproduct is a non-volatile crystalline solid, miscible in water and alcohol, and was not considered a vapor hazard. Thus no inhalation experiments were performed. The reaction is thought to occur as shown:



VX

Data at CRDEC indicates that this "bis" impurity is formed to the extent of about 10% during alcoholic base hydrolysis and is slowly hydrolyzed at pH > 13, thus even when formed it is converted to the less toxic fragments from cleavage of the P-S bond. Use of the acid chlorinolysis procedure (suitable for large scale decontamination related to Demil, but difficult to perform safely on a laboratory scale) yields a clean hydrolysis product with cleavage at the P-S bond of VX to produce decontamination products which contain no "bis" impurity and which test non-toxic in animal screens. Exposure of VX to excess base and hypochlorite (as outlined in Section 4.2.4.6) indicates that the "bis" impurity is not formed during the reaction. A solution used for toxicological tests resulting from decontamination of VX with 10% calcium hypochlorite according to the protocol given in Section 4.2.4.6 showed > 99.5% VX destroyed (nmr analysis) and the products are the expected ethyl methylphosphonic acid salt (again nmr analysis) and no "bis" impurity or "pyro" signal. This solution, when tested in the standard toxicological protocol (Section 4.3.4) is non-toxic (See also Appendix). Therefore the recommended decon for VX, as outlined in Section 4.2.4.6, is for reaction of VX with calcium hypochlorite solutions.

6.5 Chlorovinylarsine dichloride (Lewisite)

Lewisite, an arsenical vesicant produced for World War II, subjected to basic solutions decomposes to the inorganic arsenite, chloride and acetylene. Lewisite, in 10% aqueous base, is extremely fast (estimated half-life < 5 sec) and rapidly releases acetylene and inorganic arsenite according to the following reaction:

$$ClCH{=}CHAsCl_2 + 6\ NaOH \rightarrow Na_3AsO_3 + 3\ NaCl + H_2C_2 + 3\ H_20$$

The chemical literature of the early 1940's reported these studies in detail, the classic work being that of Waters and Willians (1950). The chemical literature of the organometallic arsenic compounds of Lewisite has been reviewed extensively by Doak and Freedman (Organometallic Compounds of Arsenic, Antimony and Bismuth, John Wiley & Sons, Inc., New York, 1970, p. 65, 89- 90, 103-104, 109-110). This base reaction is so rapid that it is difficult to analyze a decon solution of Lewisite rapidly enough by most analytical techniques to show any residual agent. Preparation of the decon reaction in preparation for nmr analysis immediately causes effervescence (acetylene production) followed by a spectrum that contains no Lewisite and also no organic signals (See Appendix). In all cases nmr analysis of product formation (see Appendix) confirmed earlier work showing the speed of decontamination (10 half-lives < 5 minutes). Since there has been very little interest in this agent since WWII little

recent work at CRDEC has been performed and a minimum of waste is generated.

6.6 Phenarsazine chloride (Adamsite)

We have found no record of adamsite (K996) use or decontamination at CRDEC, however, incineration appears to be the detoxification method of choice.

6.7 Bis(2-chloroethyl) sulfide (HD, Sulfur Mustard)

As stated in the review of mustard chemistry above (Section 4.1), this agent reacts with water and aqueous hydroxide at similar rates and this procedure is not considered acceptable. The only exception to this general rule is the standard use of DS2 for field expedient decontamination. This base reaction reacts rapidly with mustard to form divinyl sulfide with a half-life of < 30 sec. This solution is not usually used form deliberate decon as its capacity is low and it is extremely corrosive to equipment, although the method is fast. Since WWI the preferred way to decontaminate solutions of mustard or mustard analogues is to oxidize them with chlorine oxidants. The use hypochlorite oxidation is rapid and characterized by production of numerous products. Nitric acid oxidation, suggested in the archival literature, rapidly produces only mustard sulfoxide as its decon product. Because of expense, kinetics and ease of use hypochlorite oxidation is now the standard deliberate decon method used against mustard. Nmr analysis of mustard decontaminated with hypochlorite show at least 20 products, however, greater than 99.5% destruction of mustard. Numerous studies have shown that in the presence of excess chlorine oxidant that mustard is rapidly destroyed to multiple products which are non-toxic in the usual toxicological tests (see Appendix).

6.8 2,2'-di(3-chloroethylthio)-diethylether (T)

Agent T (K998) is a mustard and was not used as a separate filling in munitions. However, agent T is found as a mixture/solution with HD and is listed as HT. Although T has not been studied as a separate agent, its chemistry is very close to mustard and therefore all the discussion applicable for H should be comparable to T (A similar situation exists in comparison of GB with GD. Although a slightly different structure is involved the reactions are found to be very similar and usually differ only in solubility parameters and slight differences in kinetic rates.).

BLANK PAGE

7.0 Summary

In September 1987, the State of Maryland requested that CRDEC demonstrate that residues from decontamination of chemical warfare agents used in research contain no chemical agents. This information would be used to make a determination as to whether the decontamination procedures resulted in wastes than can be excluded from current regulation.

Specifically, the State of Maryland requested a detailed description of the actual decontamination procedures used on laboratory materials, including step-by-step outline of the decontamination process, identity of the specific decontaminating solution used for a given CW agent, the theoretical chemical basis for a given decontaminating action, and the concentrations, time and any other parameters that influence the degree which the reaction goes to completion. In addition, the State requested documentation that decontaminated wastes used for toxicology tests are equivalent to those resulting from the actual decontamination process and well as documentation that toxicological tests follow generally accepted practices.

In response to these issues this document supports the basic premise that these decontamination reactions are well understood and documented. Do theoretical chemical calculations support claims that agents plus decontaminants yield products that no longer contain agents? They do. Reaction energies, reaction kinetics, chemical equilibrium, laws of thermodynamics, material balance and other mathematical considerations indicate that A + B do indeed equal C + D (Section 2). In addition, product analysis procedures indicate that the quantity of CW agents remaining following decontamination are below detectable limits (Section 5) and new analytical techniques are constantly being incorporated to improve the sensitivity, accuracy and speed of these determinations.

Are older decontamination procedures, which used different reagents, equivalent to today's protocols and reagents? In most cases, yes. For example, when using sodium hydroxide or sodium carbonate, the reactive decontaminating moiety in both cases (see discussion in Section 3) is the hydroxyl ion (^{-}OH). In the search for the most efficient procedures, numerous systems have been investigated (extensively documented in Section 4.1). Over the years several procedures have been shown to be consistently efficient against a broad range of agents, and these procedures are now the accepted "standard" for routine decontamination, although the search continues for more efficient techniques. Incorporated into this document are specific examples of the procedures utilized in present decontamination procedures against listed CW agents (Section 4.2).

Do analytical results and toxicological data substantiate complete destruction of chemical agents when decontaminated? Yes. Extensive information accrued since 1918 provides incontrovertible scientific evidence of decontamination efficacy. As can be seen from the specific examples given in Section 4, information exists on procedures where the decontamination solution

are analyzed both chemically and *via* toxicological methods. Those solutions, which are certified to contain no remaining CW agents are the ones which also show minimal toxicity in toxicological examination accepted by the industrial and regulatory communities. Thus, both chemically and toxicologically, these processes have demonstrated that no CW agent remains.

The extensive decontamination experience and comprehensive data bases at CRDEC have underwritten huge demilitarization projects in the past. In all cases, decontamination and disposal projects for agent-filled munitions were executed safety, without untoward incident, and in total compliance with every prevailing environmental and human safety stricture and concern. In addition, the concern for ensuring safety has lead to adoption of large margins of safety into these procedures. Once theoretical parameters are determined, excess decontaminant is utilized as a margin of safety. Therefore, protocols today are even safer than those used in previous years. These and other facts enumerated in detail in this document provide ample evidence that current decontamination protocols and procedures are safe, scientific, and result in the total destruction of chemical agents.

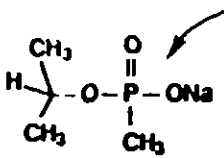
APPENDIX

8.1 NMR Data

8.1.1 GB Hydrolysis in 10% NaOH

Experimental Conditions: 0.02 mL of GB in 1 mL of 10% NaOH (2.5N): pH > 14
Sample miscible with shaking.

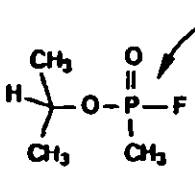
Results: Spectrum at ~ 10 min shows only:



^{31}P at 26.3 ppm

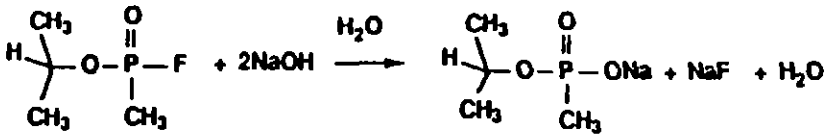
Upper Trace: Hydrolysis Product

Lower Trace: GB Starting Material

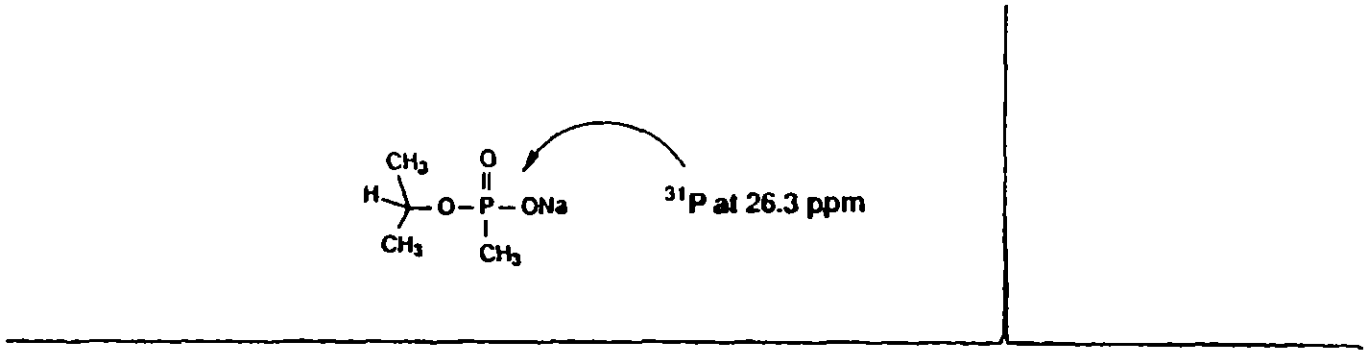


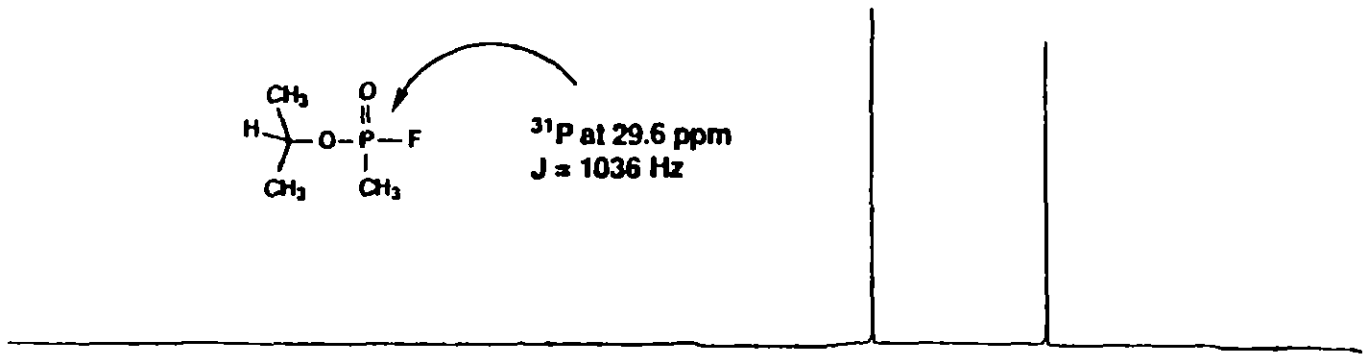
^{31}P at 29.6 ppm
J = 1036 Hz

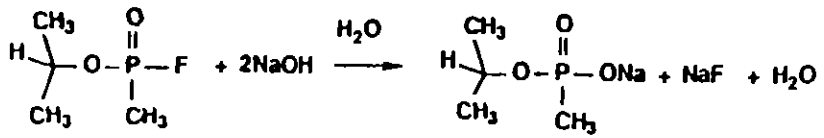
Hydrolysis Stoichiometry:



8.1.1 GB Hydrolysis in 10% NaOH



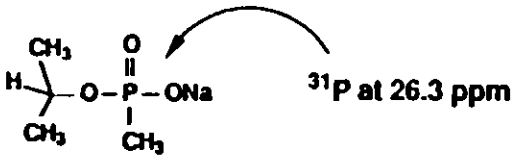




8.1.2 GB Hydrolysis in 10% Na_2CO_3

Experimental Conditions: 0.02 mL of GB in 1 mL of 10% Na_2CO_3 (2.0N): pH 12.2
Sample miscible with shaking.

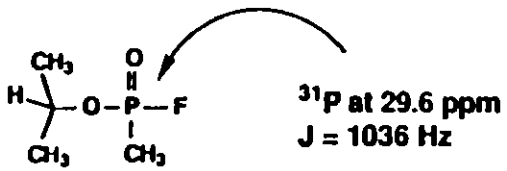
Results: Spectrum at ~ 5 min shows only:



^{31}P at 26.3 ppm

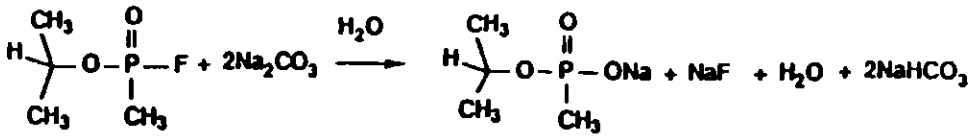
Upper Trace: Hydrolysis Product

Lower Trace: GB Starting Material

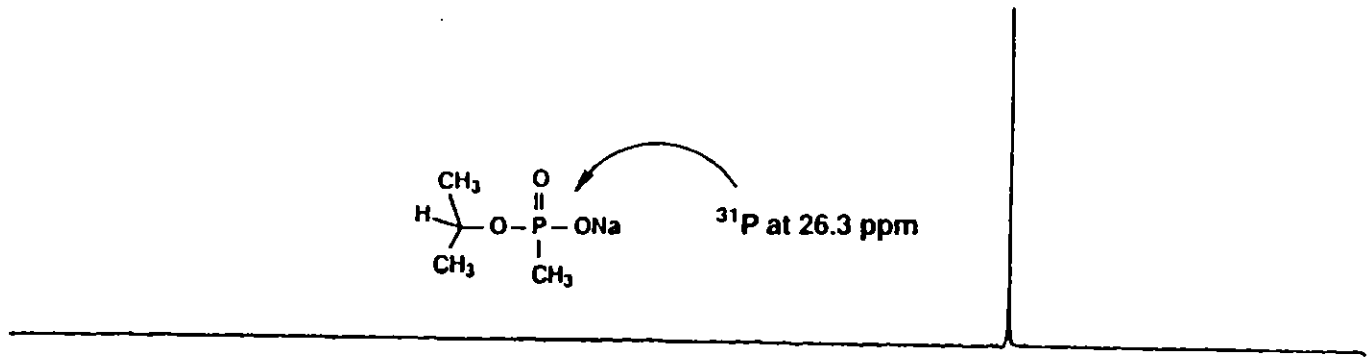


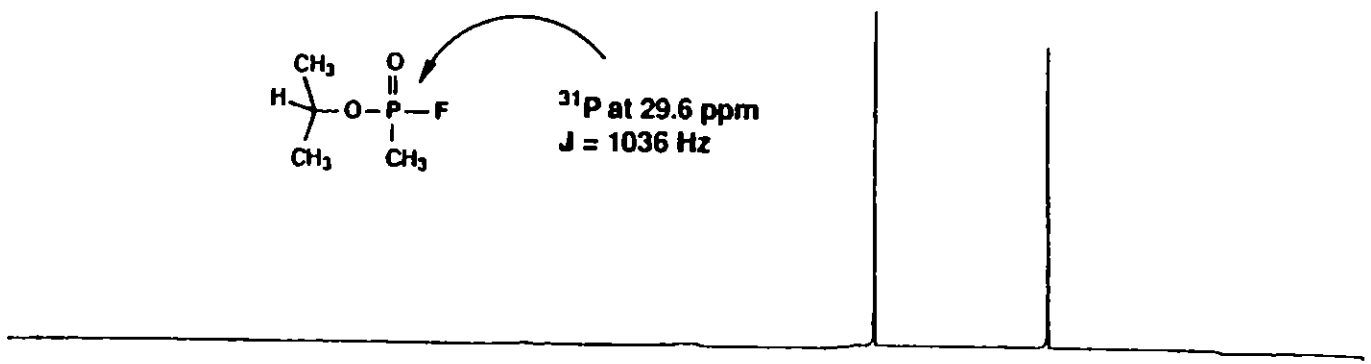
^{31}P at 29.6 ppm
J = 1036 Hz

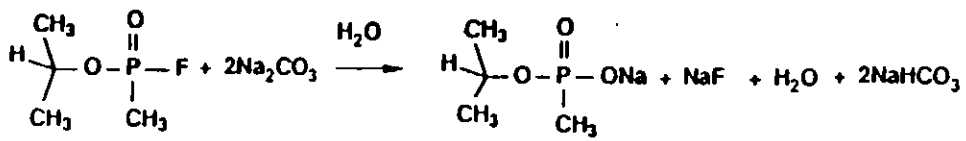
Hydrolysis Stoichiometry:



8.1.2 GB Hydrolysis in 10% Na_2CO_3



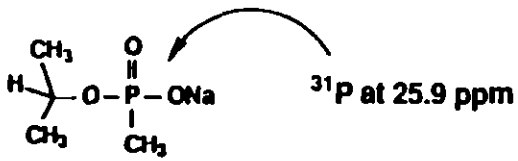




8.1.3 GB Hydrolysis in 10% Alcoholic NaOH

Experimental Conditions: 0.02 mL of GB in 1 mL of 10% Alcoholic NaOH (2.5N): pH > 14
Sample miscible with shaking.

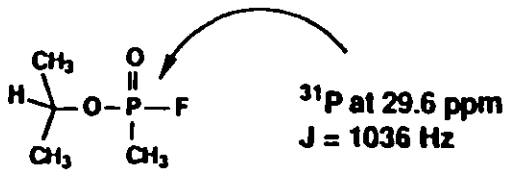
Results: Spectrum at ~ 10 min shows only:



^{31}P at 25.9 ppm

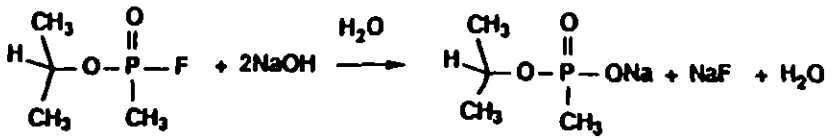
Upper Trace: Hydrolysis Product

Lower Trace: GB Starting Material

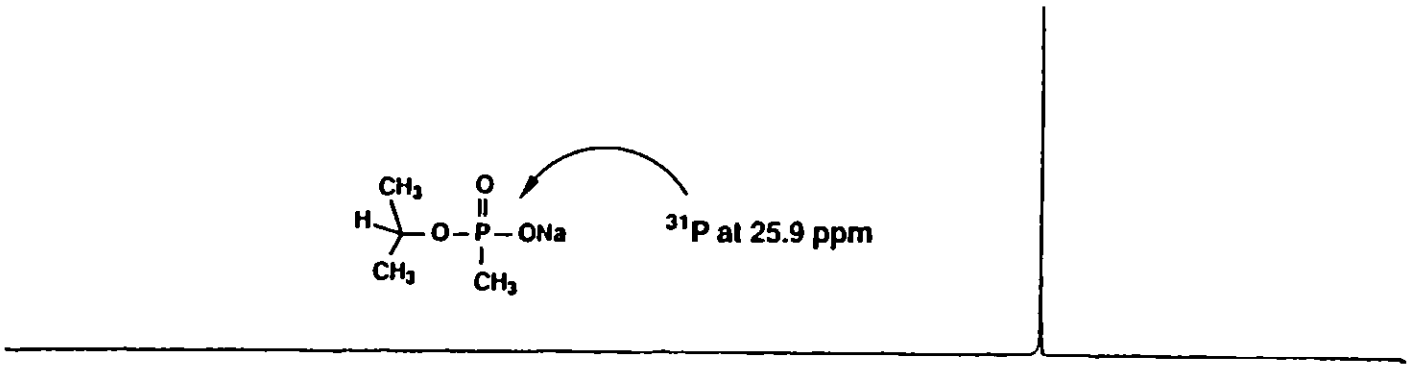


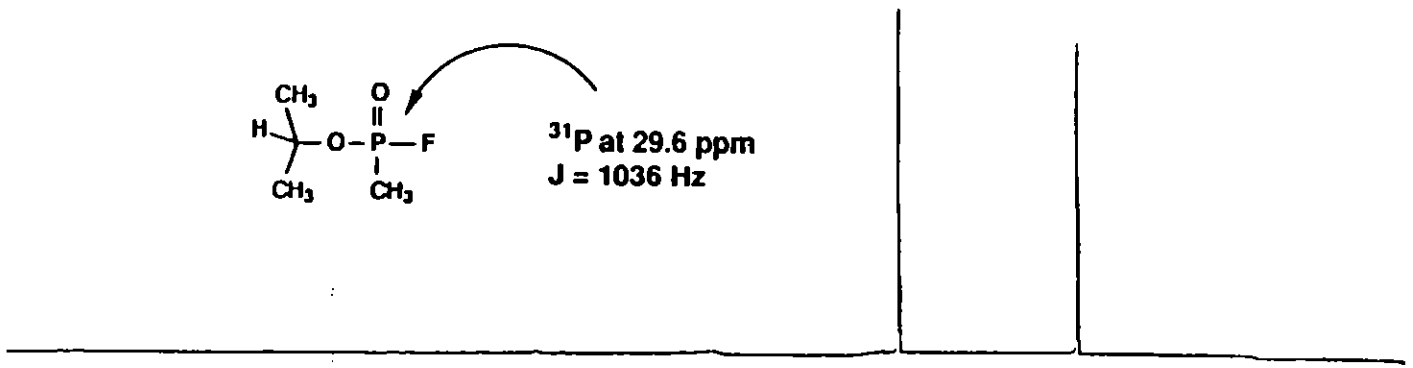
^{31}P at 29.6 ppm
J = 1036 Hz

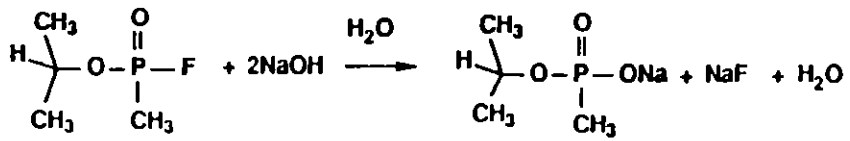
Hydrolysis Stoichiometry:



8.1.3 GB Hydrolysis in 10% Alcoholic NaOH



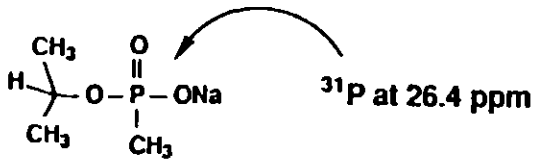




8.1.4 GB Hydrolysis in 5.25% NaOCl

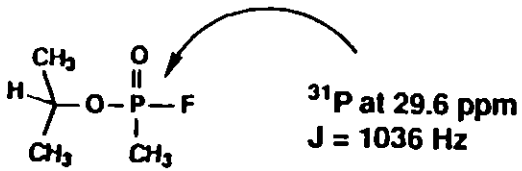
Experimental Conditions: 0.02 mL of GB in 1 mL of 5.25% NaOCl : Sample miscible with shaking.

Results: Spectrum at ~ 5 min shows only:

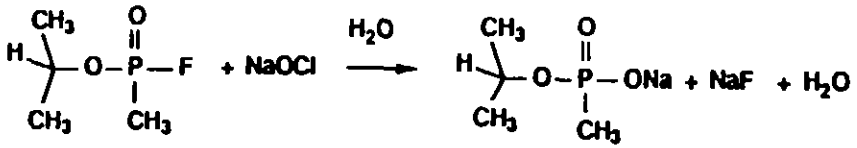


Upper Trace: Hydrolysis Product

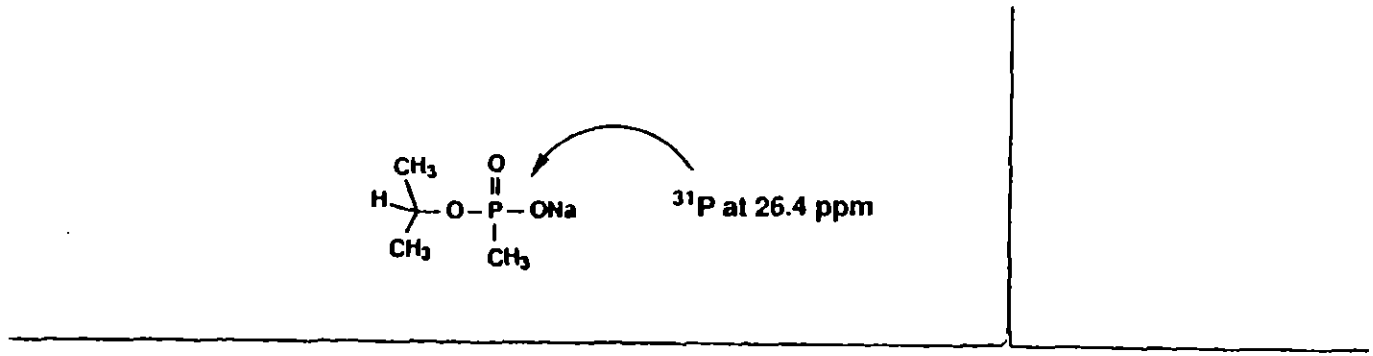
Lower Trace: GB Starting Material

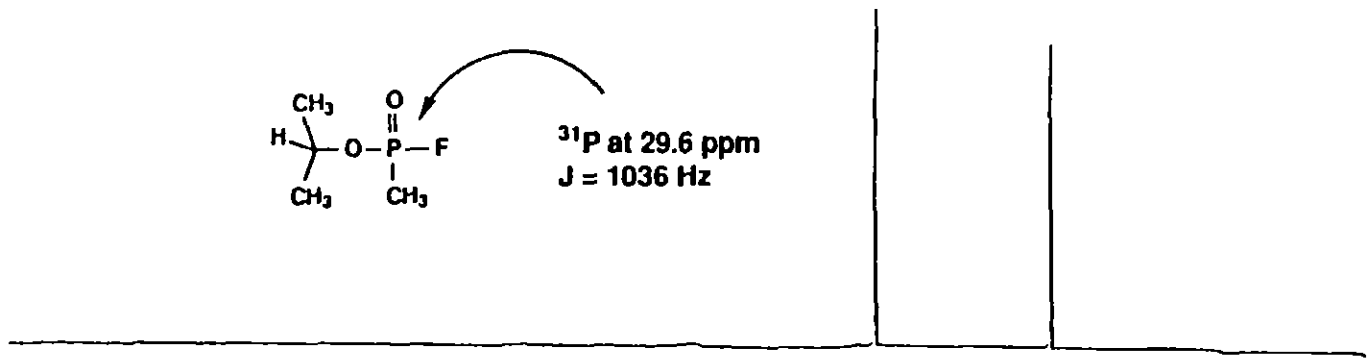


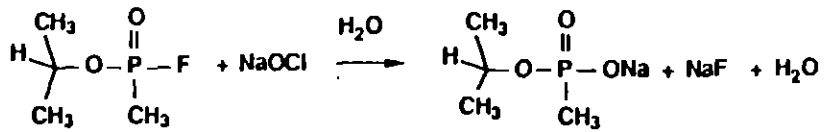
Hydrolysis Stoichiometry:



8.1.4 GB Hydrolysis in 5.25% NaOCl



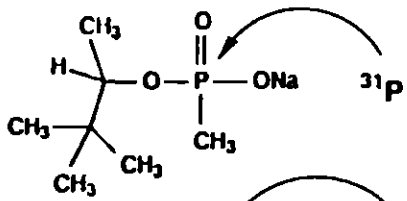




8.1.5 GD Hydrolysis in 10% NaOH

Experimental Conditions: *0.02 mL of GD in 1 mL of 10% NaOH (2.5N): pH > 14*
Sample miscible with shaking.

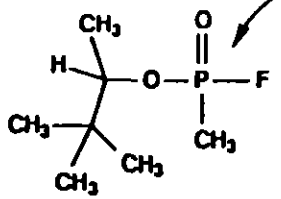
Results: Spectrum at ~ 5 min shows only:



^{31}P at 26.0 ppm

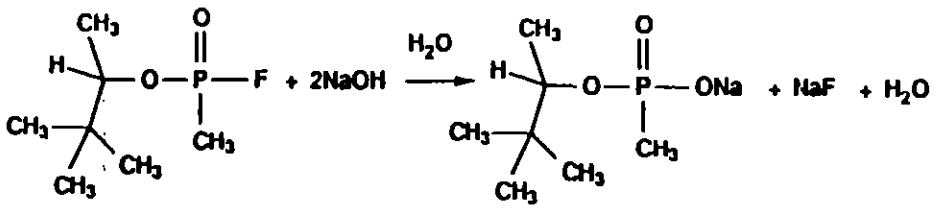
Upper Trace: Hydrolysis Product

Lower Trace: GD Starting Material

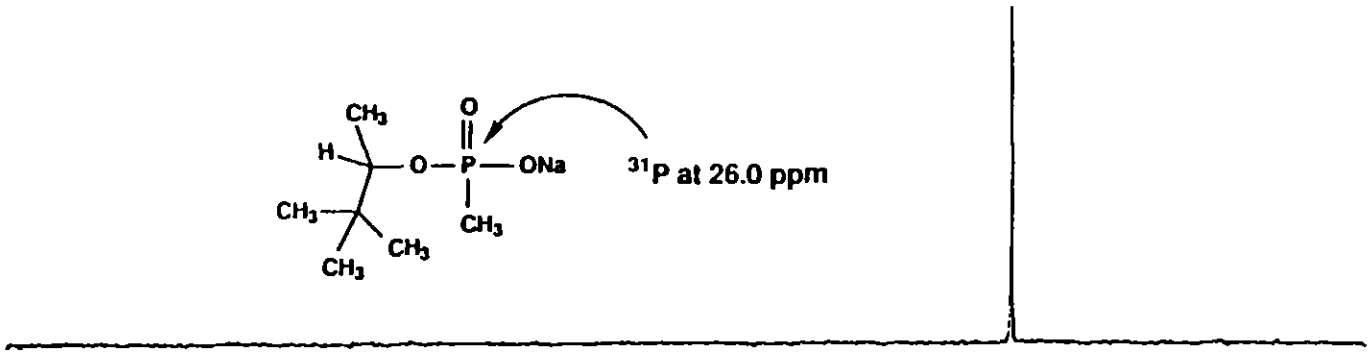


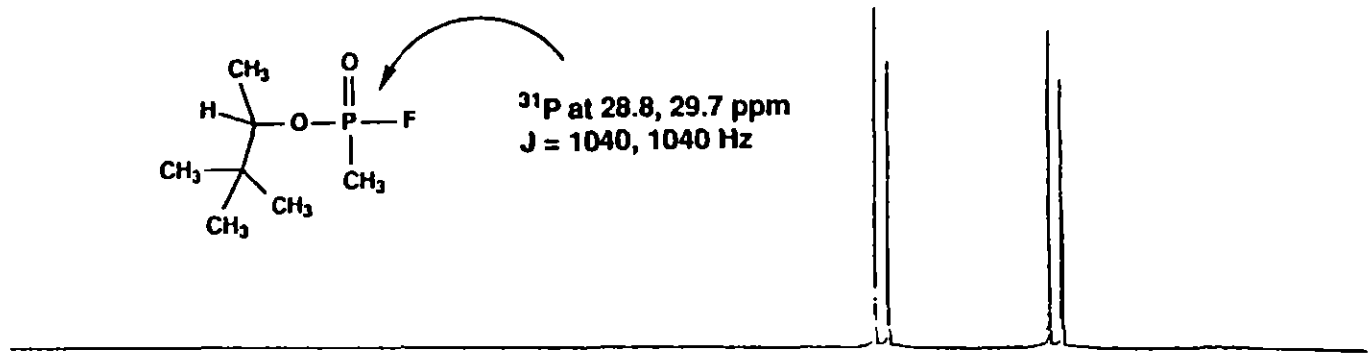
^{31}P at 28.8, 29.7 ppm
J = 1040, 1040 Hz

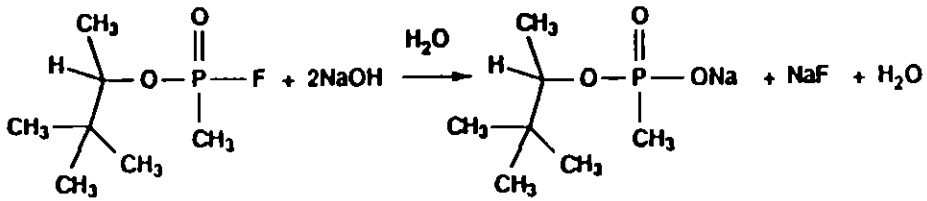
Hydrolysis Stoichiometry:



8.1.5 GD Hydrolysis in 10% NaOH



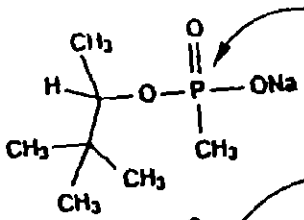




8.1.6 GD Hydrolysis in 10% Na_2CO_3

Experimental Conditions: 0.02 mL of GD in 1 mL of 10% Na_2CO_3 (2.0N): pH 12.2
Sample miscible with shaking.

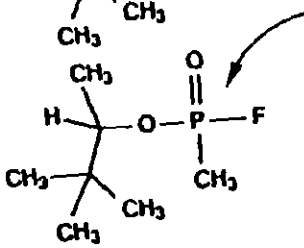
Results: Spectrum at ~ 5 min shows only:



^{31}P at 26.0 ppm

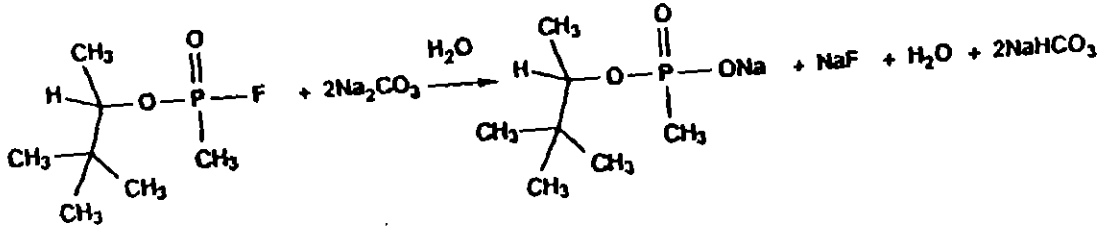
Upper Trace: Hydrolysis Product

Lower Trace: GD Starting Material

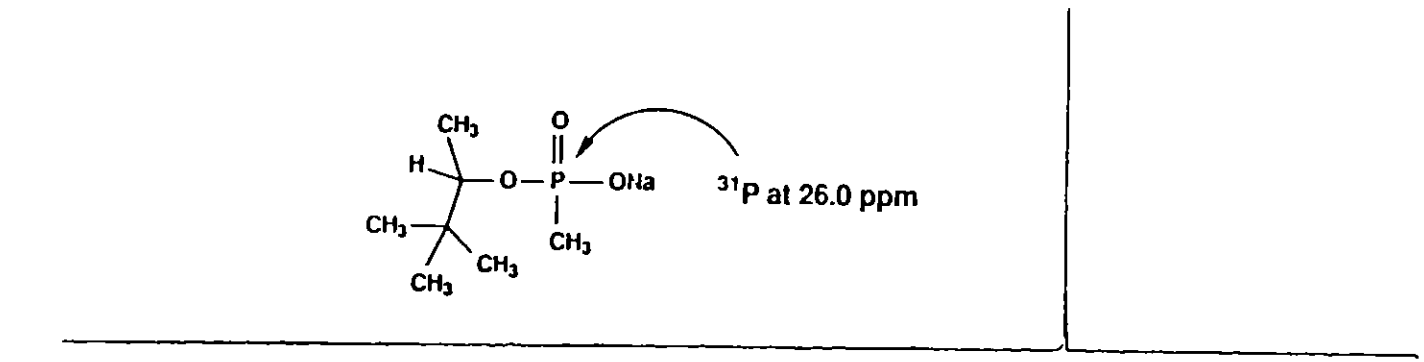


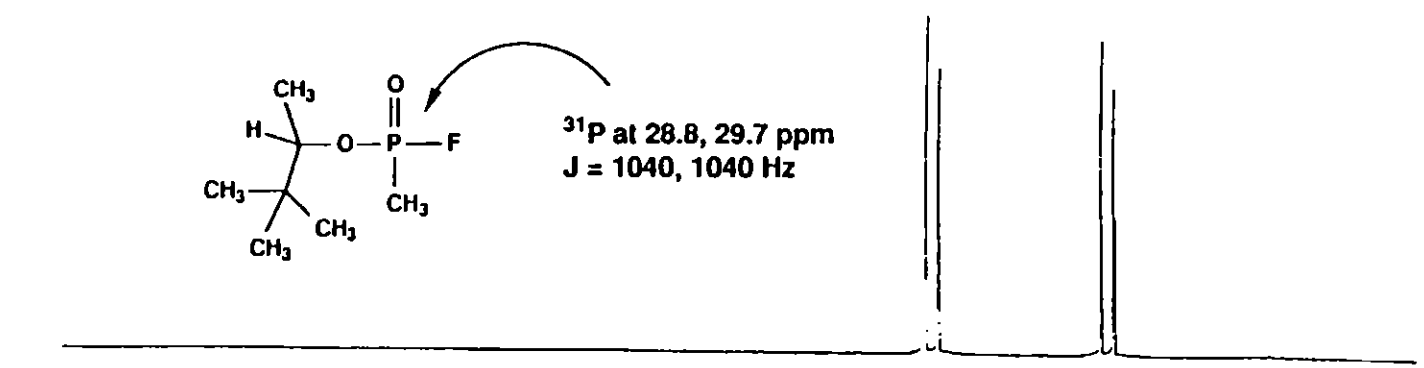
^{31}P at 28.8, 29.7 ppm
J = 1040, 1040 Hz

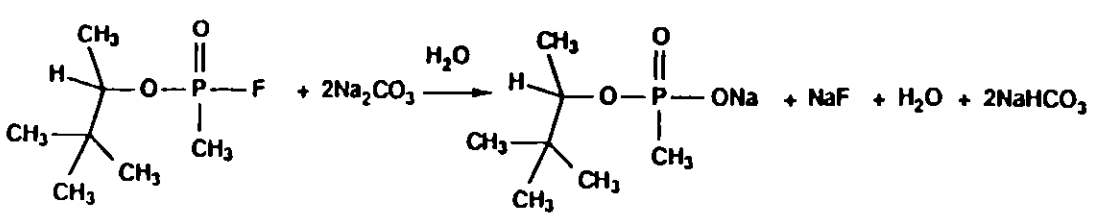
Hydrolysis Stoichiometry:



8.1.6 GD Hydrolysis in 10% Na_2CO_3



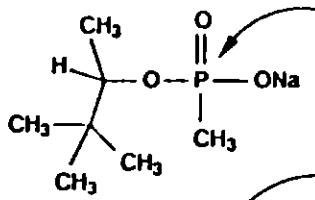




8.1.7 GD Hydrolysis in 10% Alcoholic NaOH

Experimental Conditions: 0.02 mL of GD in 1 mL of 10% Alcoholic NaOH (2.5N): pH > 14
Sample miscible with shaking.

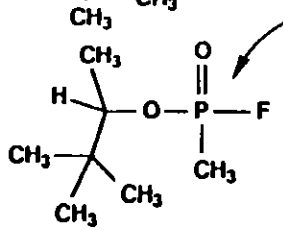
Results: Spectrum at ~ 5 min shows only:



^{31}P at 25.6 ppm

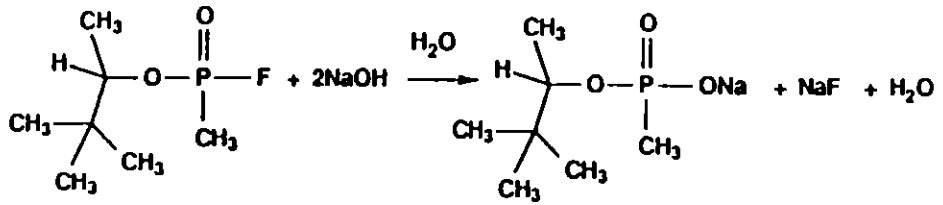
Upper Trace: Hydrolysis Product

Lower Trace: GD Starting Material

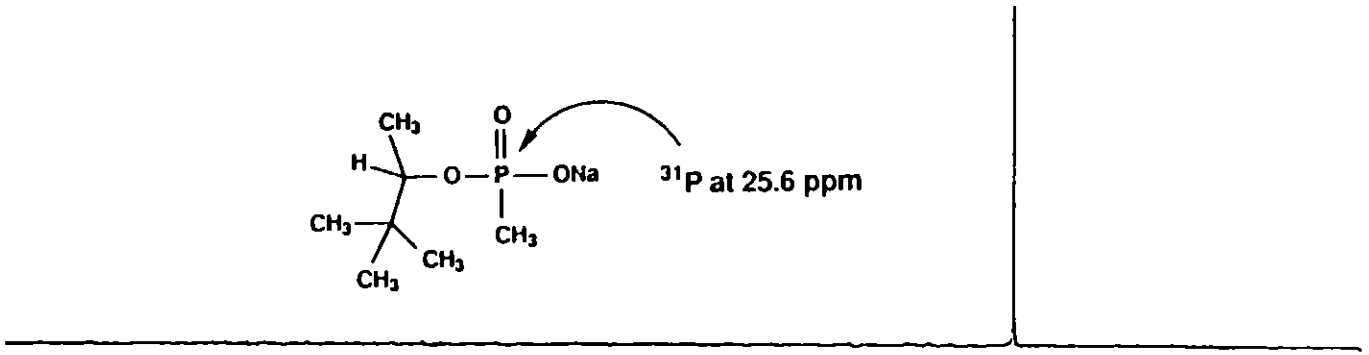


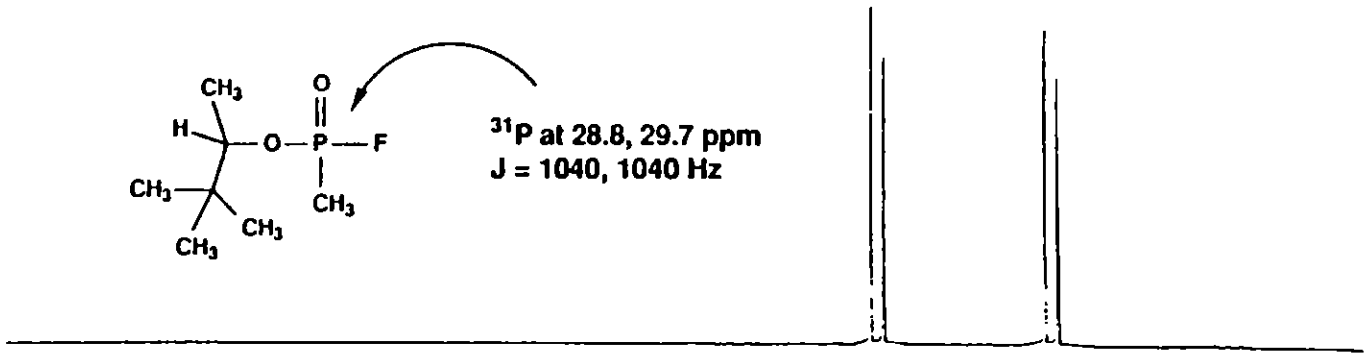
^{31}P at 28.8, 29.7 ppm
J = 1040, 1040 Hz

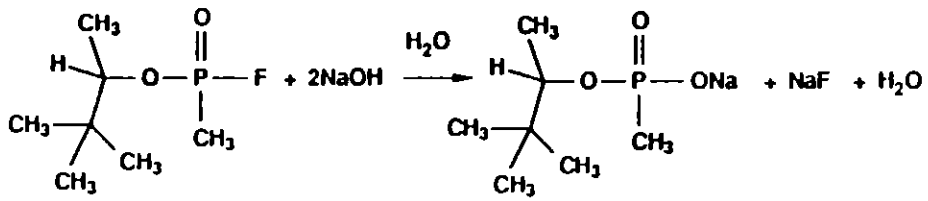
Hydrolysis Stoichiometry:



8.1.7 GD Hydrolysis in 10% Alcoholic NaOH



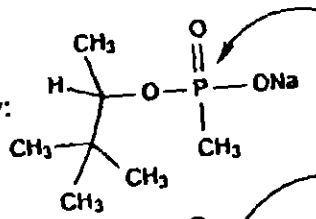




8.1.8 GD Hydrolysis in 5.25% NaOCl

Experimental Conditions: 0.02 mL of GD in 1 mL of 5.25% NaOCl:
Sample miscible with shaking.

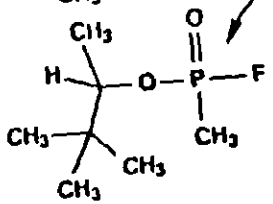
Results: Spectrum at – 10 min shows only:



^{31}P at 26.2 ppm

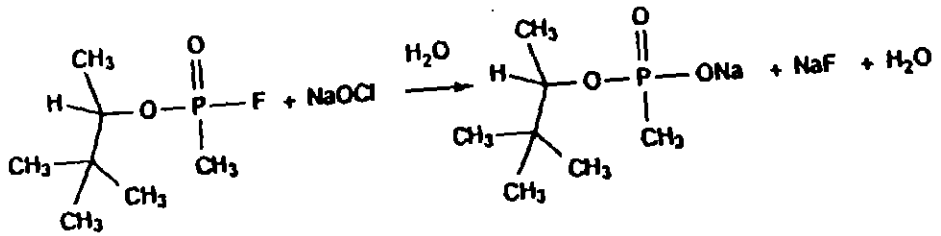
Upper Trace: Hydrolysis Product

Lower Trace: GD Starting Material

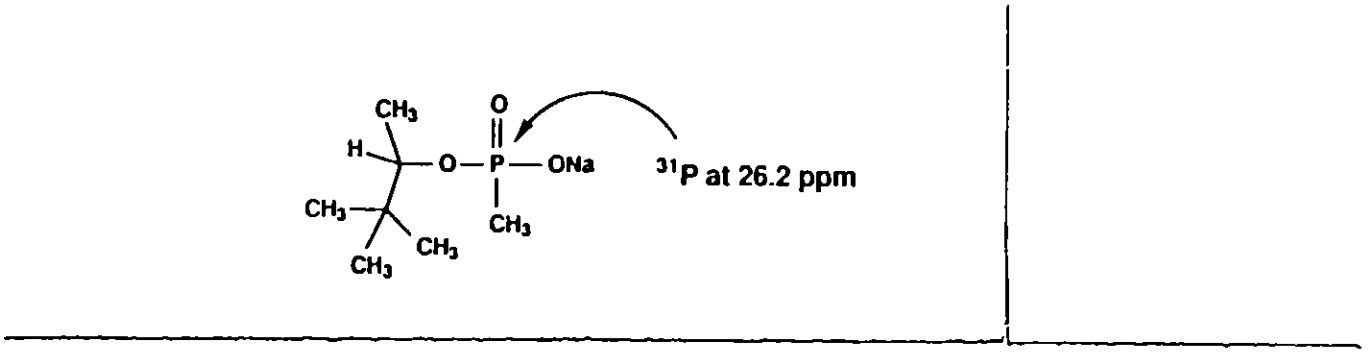


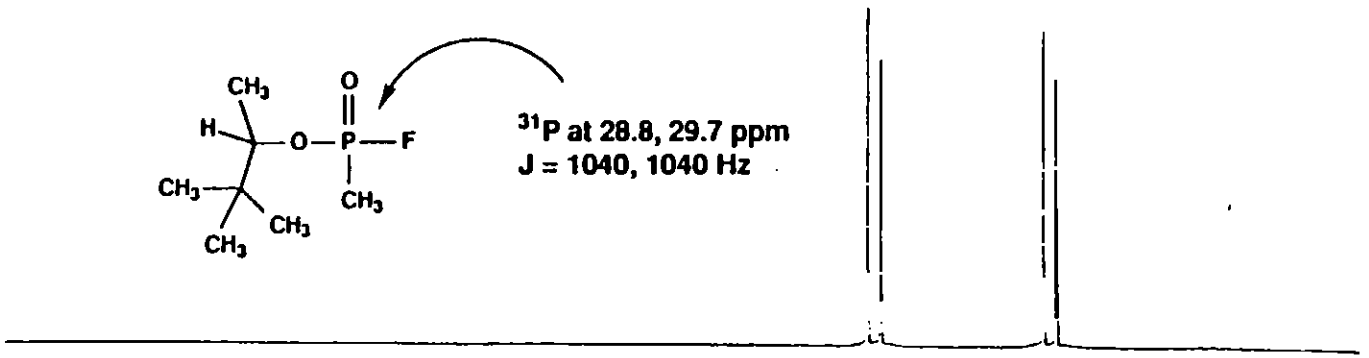
^{31}P at 28.8, 29.7 ppm
J = 1040, 1040 Hz

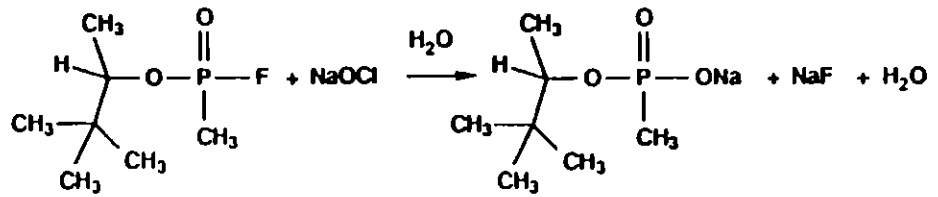
Hydrolysis Stoichiometry:



8.1.8 GD Hydrolysis in 5.25% NaOCl



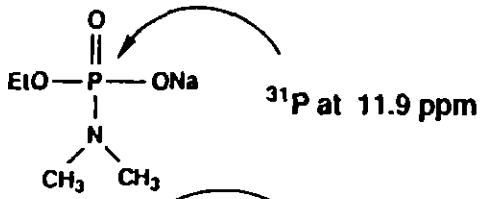




8.1.9 GA Hydrolysis in 10% NaOH

Experimental Conditions: 0.02 mL of GA in 1 mL of 10% NaOH (2.5N): pH > 14
Sample miscible with shaking.

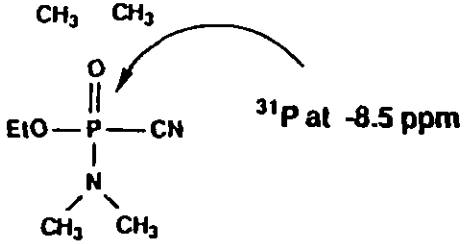
Results: Spectrum at ~ 30 min shows only:



^{31}P at 11.9 ppm

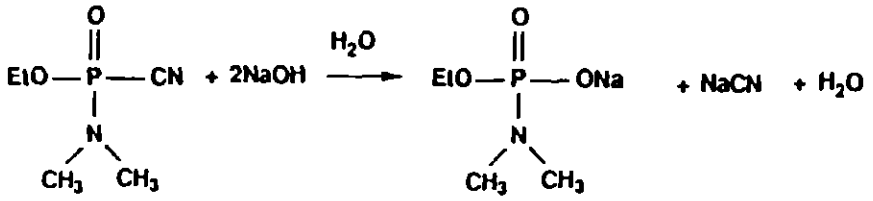
Upper Trace: Hydrolysis Product

Lower Trace: GA Starting Material

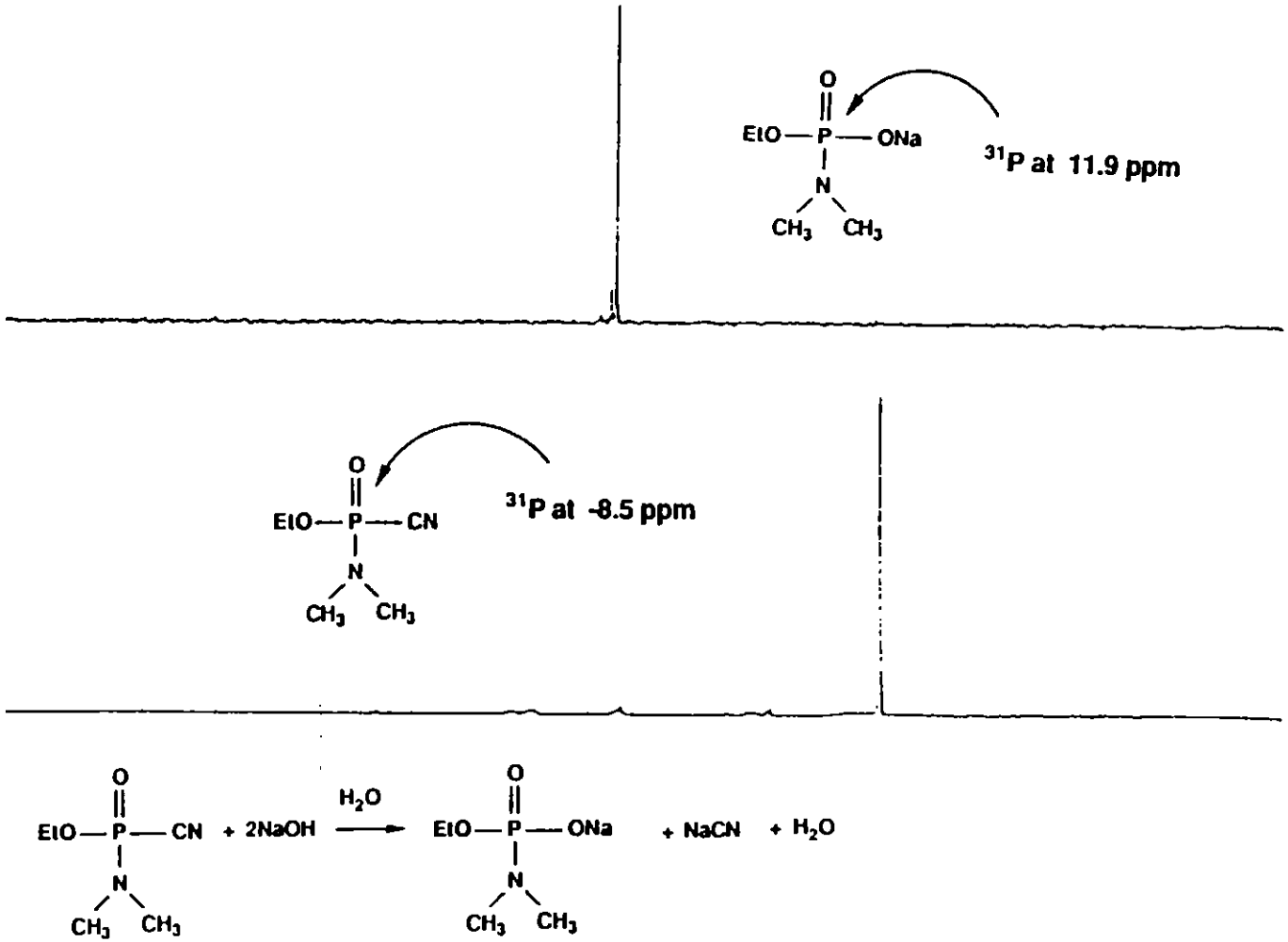


^{31}P at -8.5 ppm

Hydrolysis Stoichiometry:



8.1.9 GA Hydrolysis in 10% NaOH

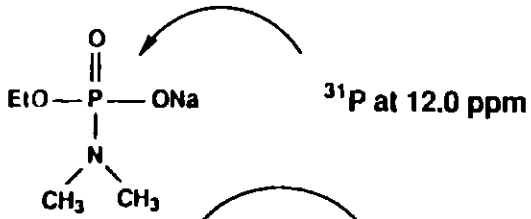


$$\text{EtO}-\text{P}(=\text{O})(\text{CN})-\text{N}(\text{CH}_3)_2 + 2\text{NaOH} \xrightarrow{H_2O} \text{EtO}-\text{P}(=\text{O})(\text{ONa})-\text{N}(\text{CH}_3)_2 + \text{NaCN} + H_2O$$

8.1.10 GA Hydrolysis in 10% Na_2CO_3

Experimental Conditions: 0.02 mL of GD in 1 mL of 10% Na_2CO_3 (2.0N): pH 12.2
Sample miscible with shaking.

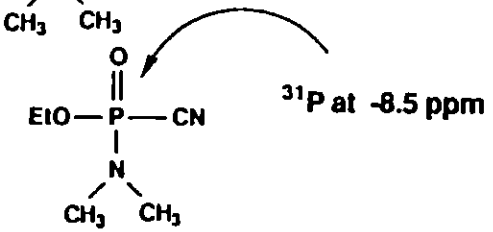
Results: Spectrum at ~ 5 min shows only:



^{31}P at 12.0 ppm

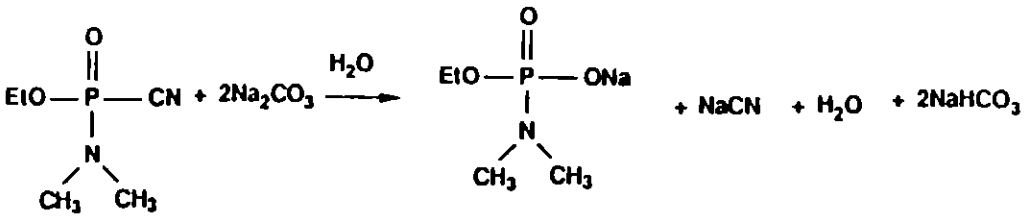
Upper Trace: Hydrolysis Product

Lower Trace: GA Starting Material

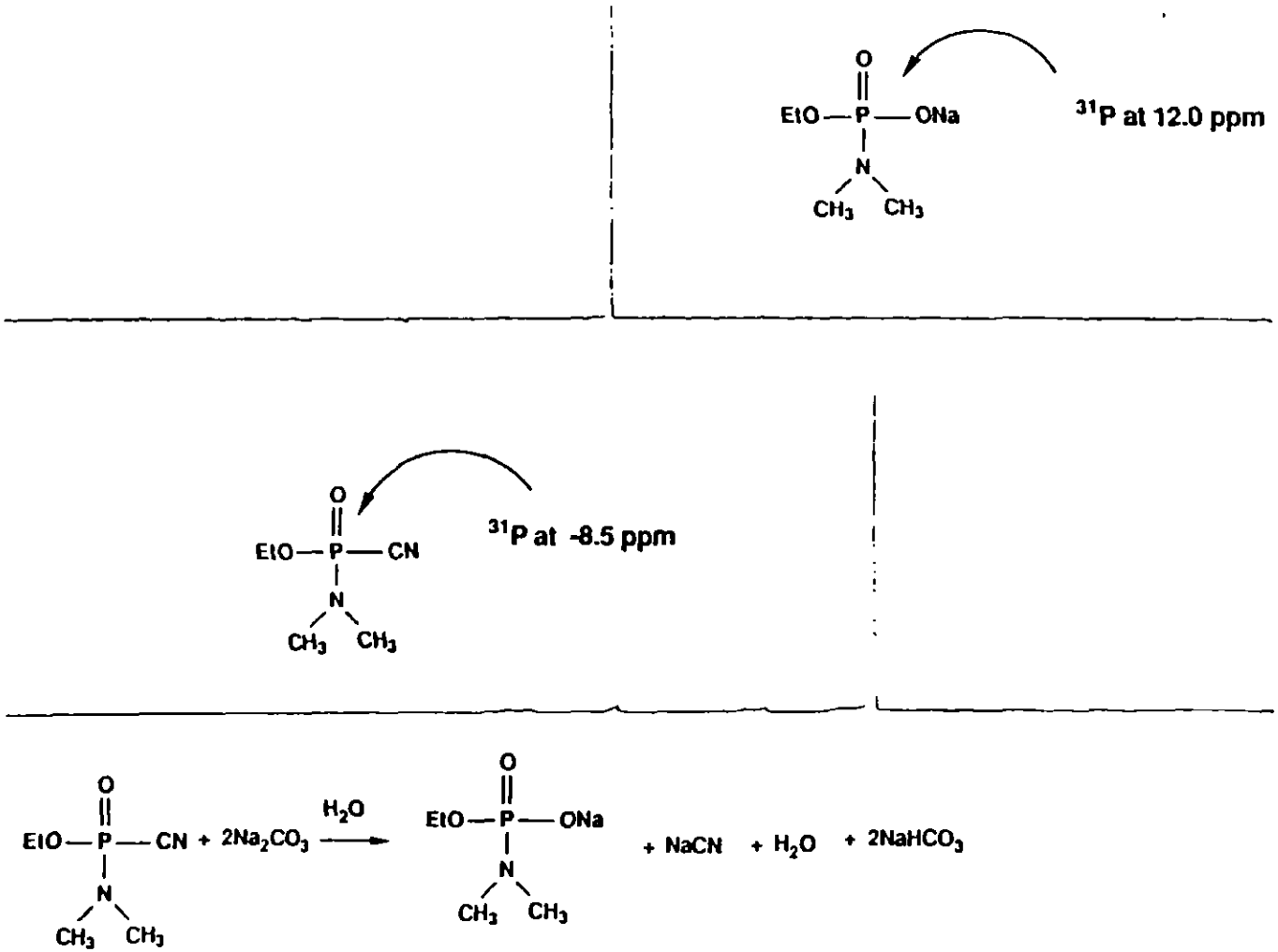


^{31}P at -8.5 ppm

Hydrolysis Stoichiometry:



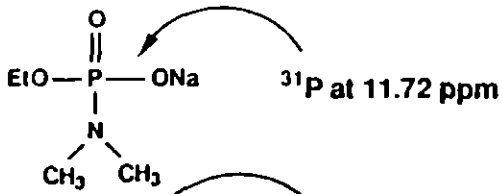
8.1.10 GA Hydrolysis in 10% Na_2CO_3



8.1.11 GA Hydrolysis in 10% Alcoholic NaOH

Experimental Conditions: 0.02 mL of GA in 1 mL of 10% Alcoholic NaOH (2.5N): pH > 14
Sample miscible with shaking.

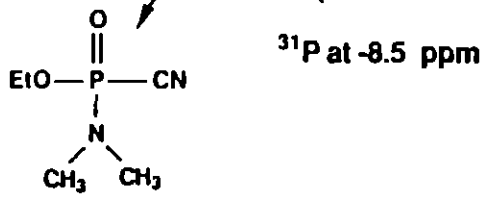
Results: Spectrum at ~ 30 min shows only:



^{31}P at 11.72 ppm

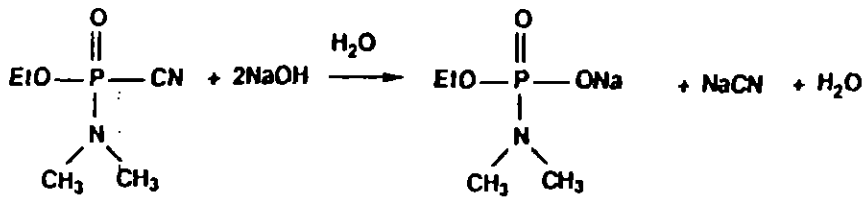
Upper Trace: Hydrolysis Product

Lower Trace: GA Starting Material

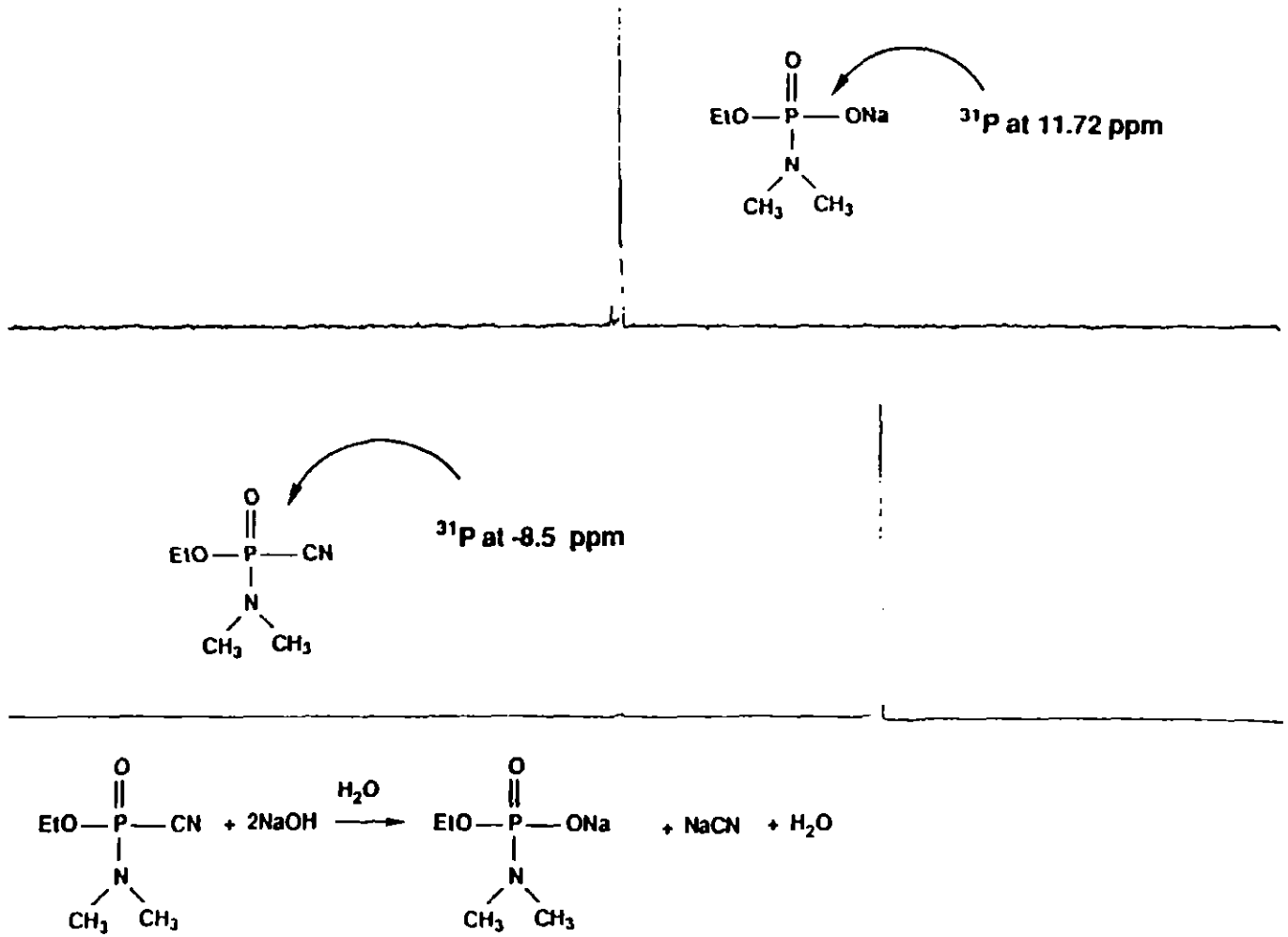


^{31}P at -8.5 ppm

Hydrolysis Stoichiometry:



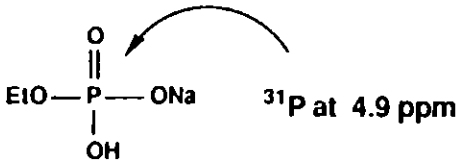
8.1.11 GA Hydrolysis in 10% Alcoholic NaOH



8.1.12 GA Hydrolysis in 5.25% NaOCl

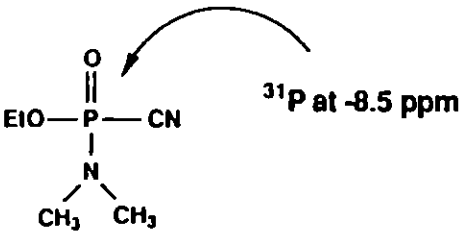
Experimental Conditions: 0.02 mL of GA in 1 mL of 5.25% NaOCl: Sample miscible with shaking.

Results: Spectrum at ~ 5 min shows only:

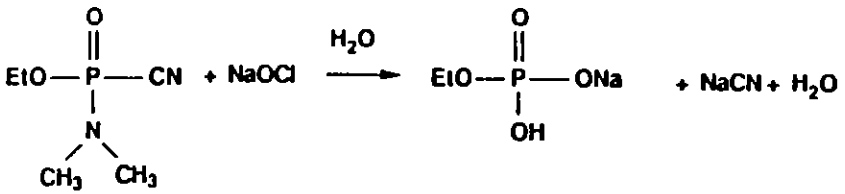


Upper Trace: Hydrolysis Product

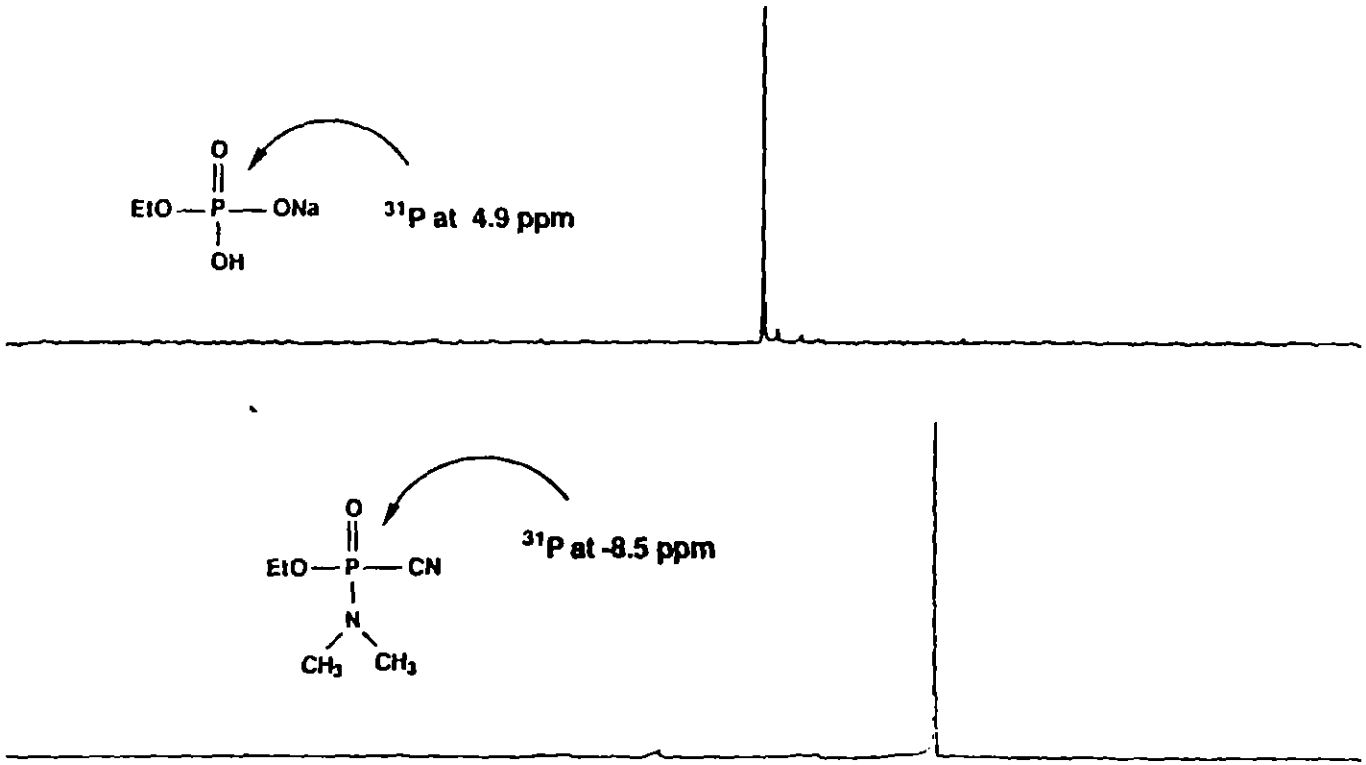
Lower Trace: GA Starting Material

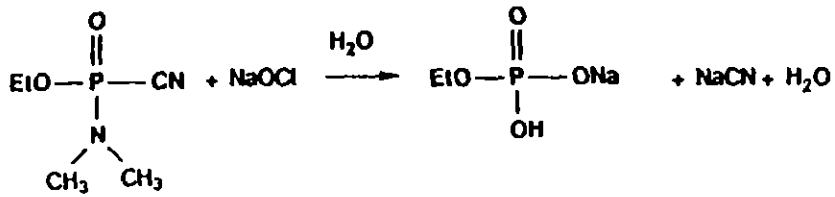


Hydrolysis Stoichiometry:



8.1.12 GA Hydrolysis in 5.25% NaOCl

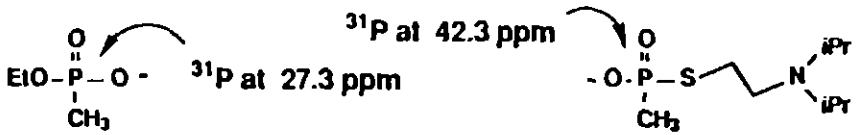




8.1.13 VX Hydrolysis in 10% Alcoholic NaOH

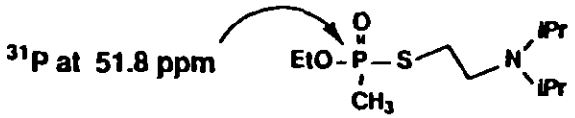
Experimental Conditions: 0.02 mL of VX in 1.5 mL of 10% Alcoholic NaOH (2.5N): pH > 14
Sample miscible with shaking.

Results: Spectrum at ~ 25 min shows:

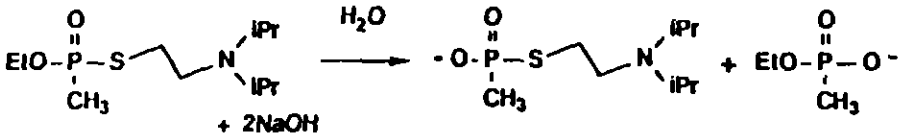


Upper Trace: Hydrolysis Product

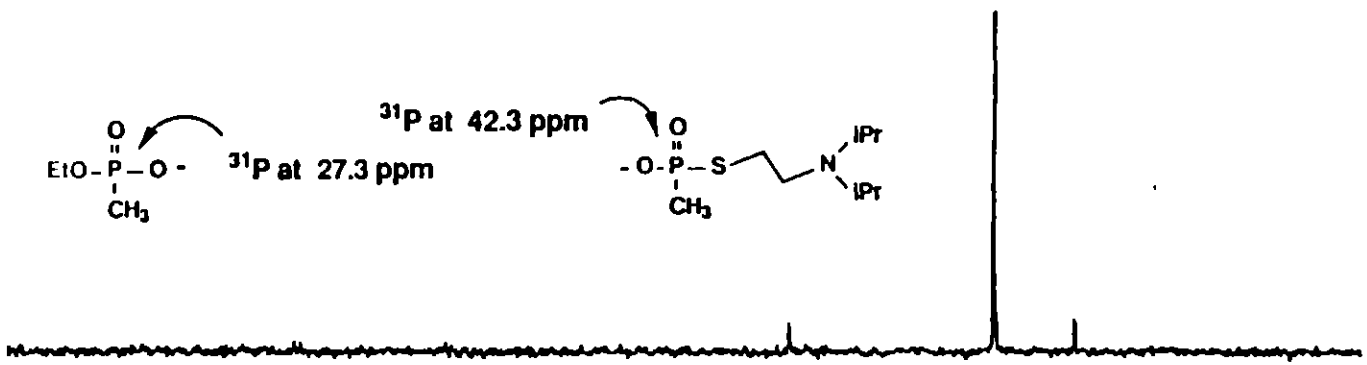
Lower Trace: VX Starting Material

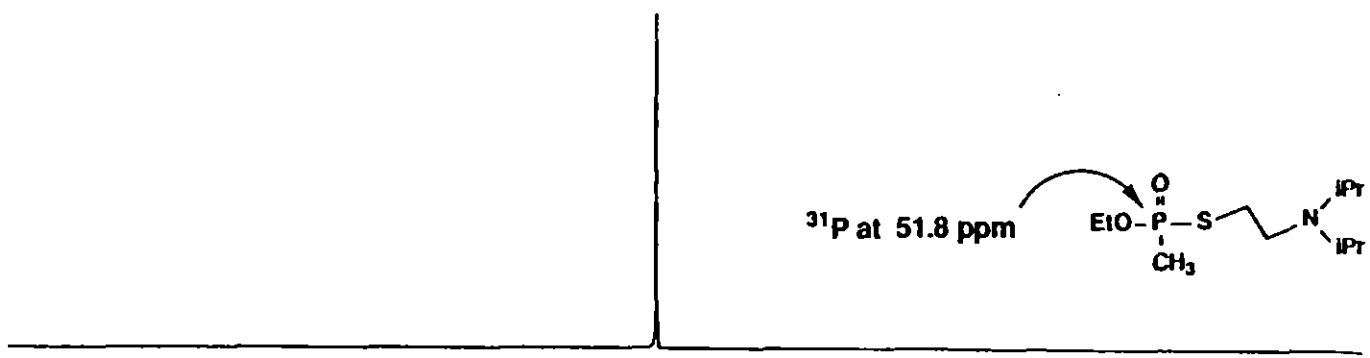


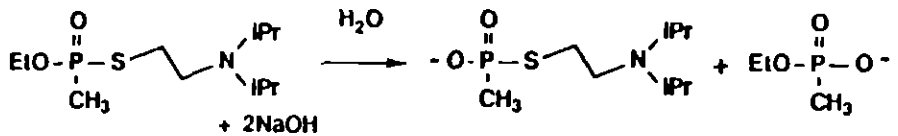
Hydrolysis Stoichiometry:



8.1.13 VX Hydrolysis in 10% Alcoholic NaOH



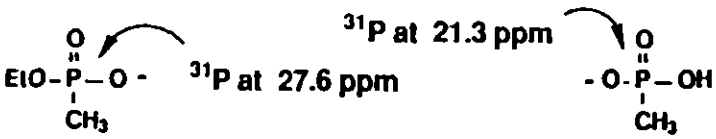




8.1.14 VX Hydrolysis in 5.25% NaOCl

Experimental Conditions: 0.02 mL of VX in 1.0 mL of 5.25% NaOCl : Sample miscible with shaking.

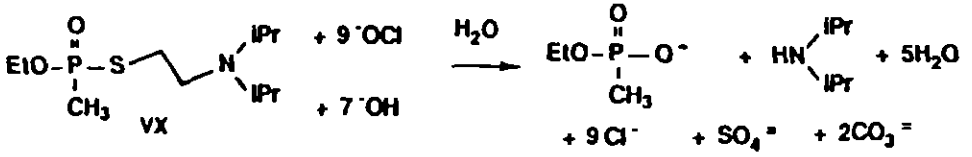
Results: Spectrum at ~ 18 Hr shows:



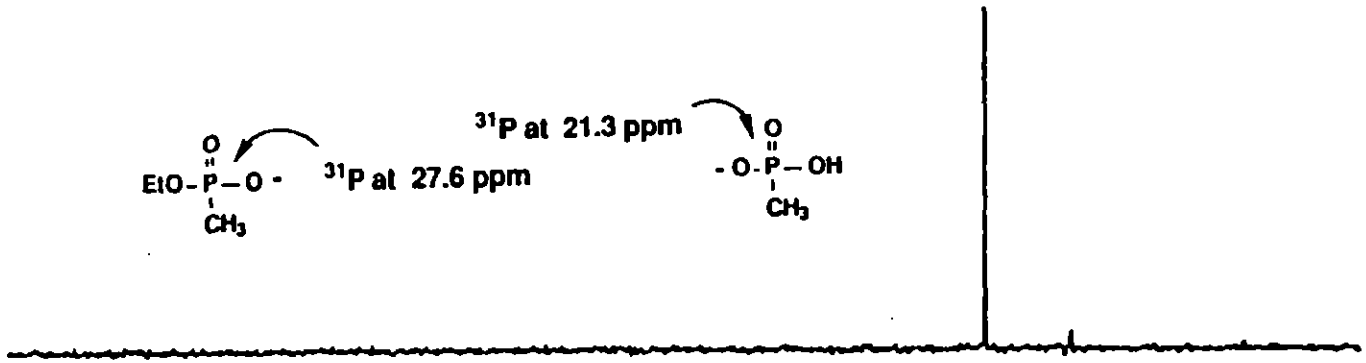
Upper Trace: Hydrolysis Product

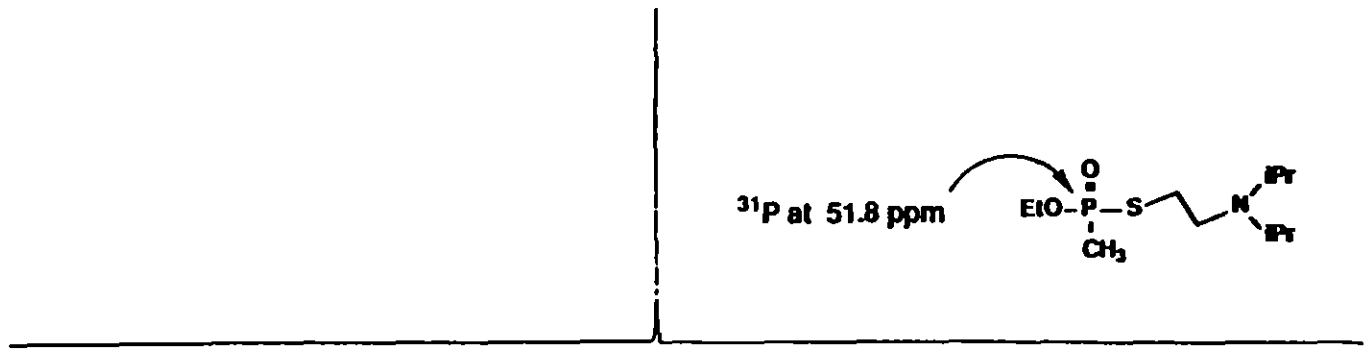
Lower Trace: VX Starting Material

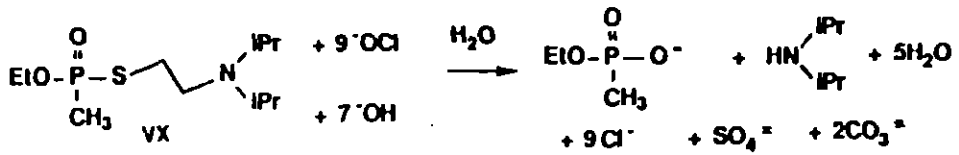
Hydrolysis Stoichiometry:



8.1.14 VX Hydrolysis in 5.25% NaOCl



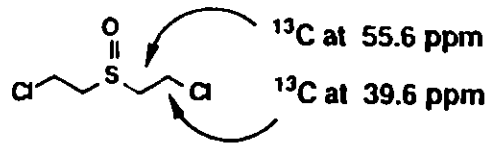




8.1.15 HD Oxidation in Conc. HNO_3

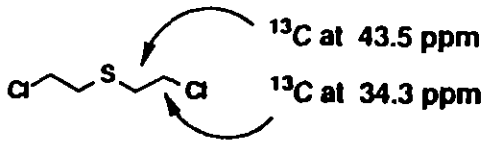
Experimental Conditions: 0.02 mL of HD in 1 mL of Conc. HNO_3: Sample miscible with shaking.

Results: Spectrum shows only:

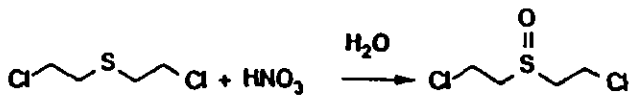


Upper Trace: Oxidation Product

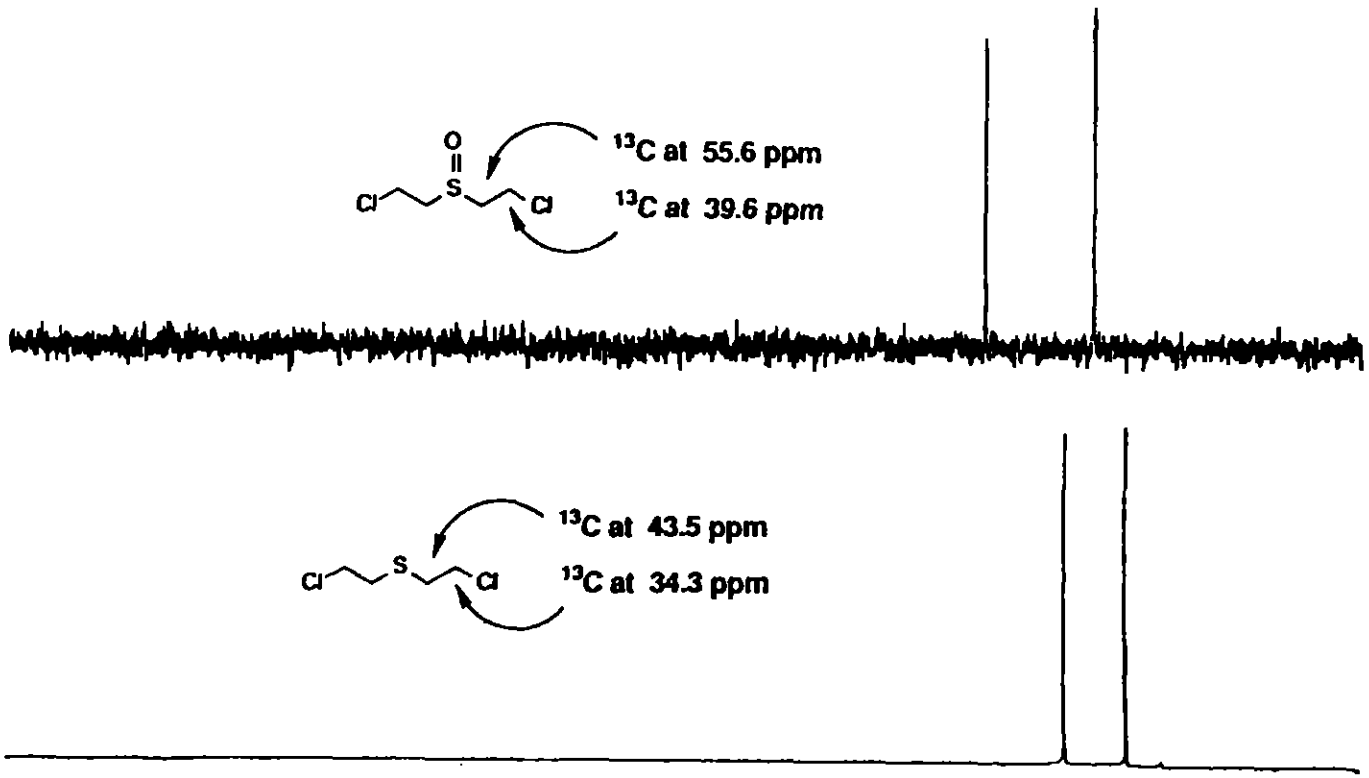
Lower Trace: HD Starting Material

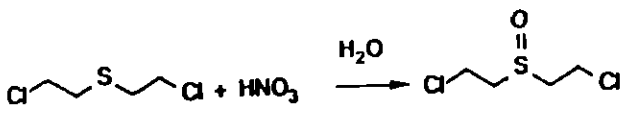


Hydrolysis Stoichiometry:



8.1.15 HD Oxidation in Conc. HNO_3



Hydrolysis Stoichiometry: 

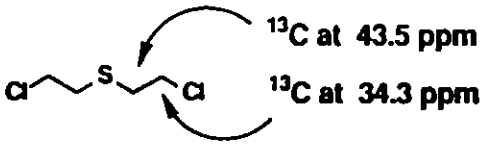
8.1.16 HD Oxidation in 5.25% NaOCl

Experimental Conditions: 0.02 mL of HD in 1 mL of 5.25% NaOCl: Sample miscible with shaking.

Results: Spectrum shows multiple oxidation products - no HD present:

Upper Trace: Oxidation Product

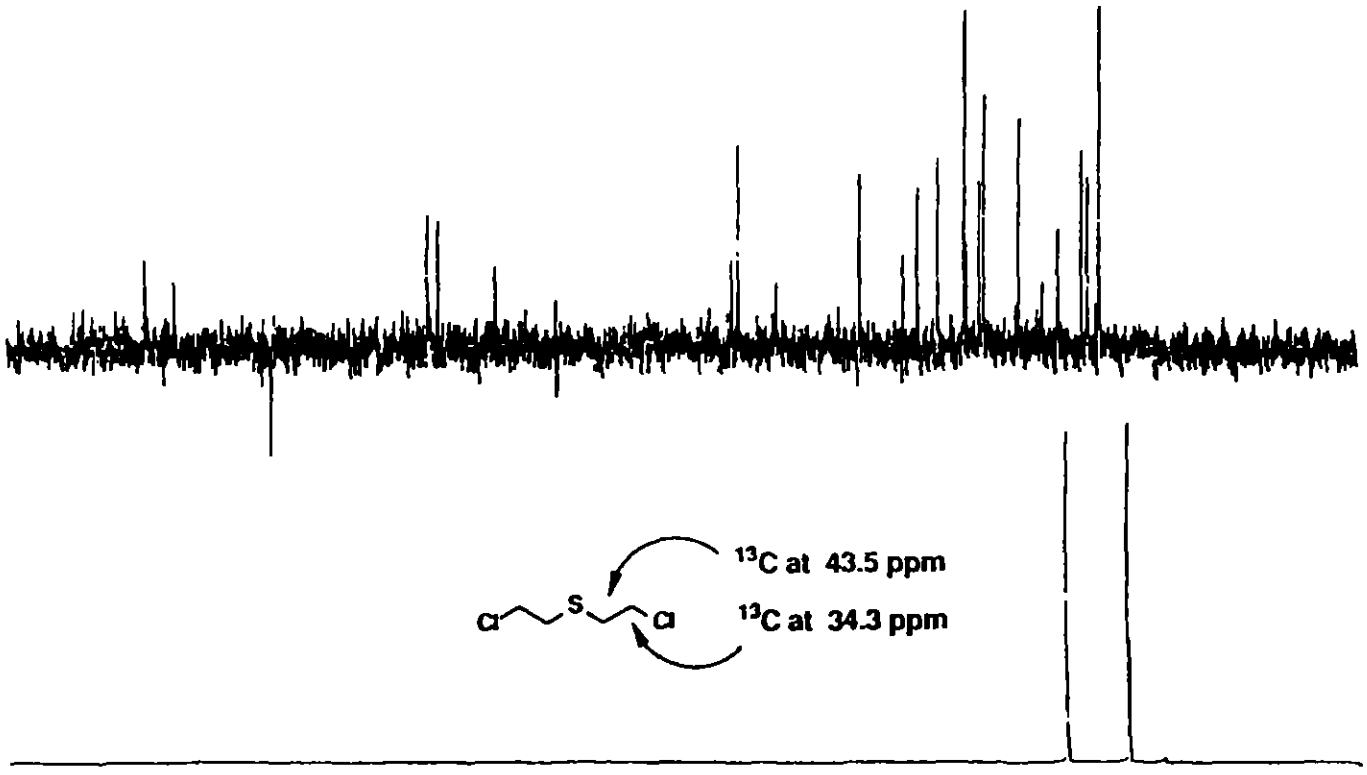
Lower Trace: HD Starting Material



Hydrolysis Stoichiometry: 

Multiple Oxidation Products

8.1.16 HD Oxidation in 5.25% NaOCl



Hydrolysis Stoichiometry:  + NaOCl $\xrightarrow{H_2O}$ Multiple Oxidation Products

8.1.17 Lewisite Hydrolysis in 5.25% NaOCl

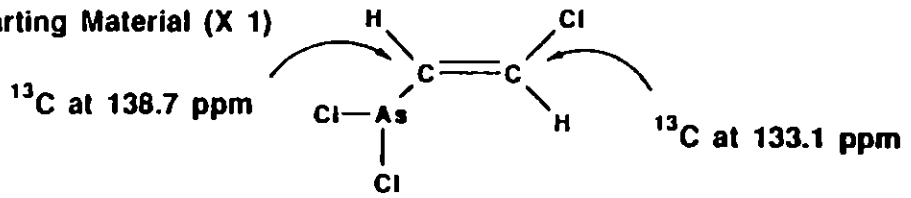
Experimental Conditions: 0.02 mL of Lewisite in 1.0 mL of 5.25% NaOCl : Sample miscible with shaking; a lot of gas (e.g., acetylene) evolved (spectrum amplitude of product (middle trace) increased X100 (top trace) to show trace peaks).

Results: Spectrum at 10 min shows: No Lewisite present; virtually no signal at all. Sample appears to have reacted to give acetylene (gas).

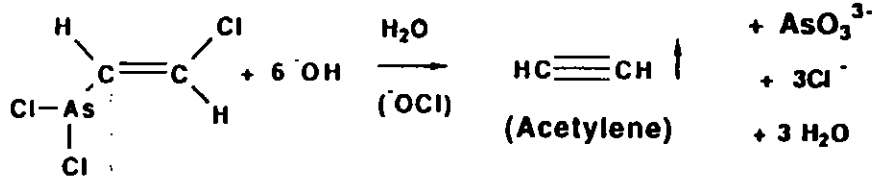
Upper Trace: Hydrolysis Product (X 100)
Middle Trace: Hydrolysis Product (X 1)

No Carbon: Thus no spectral lines.

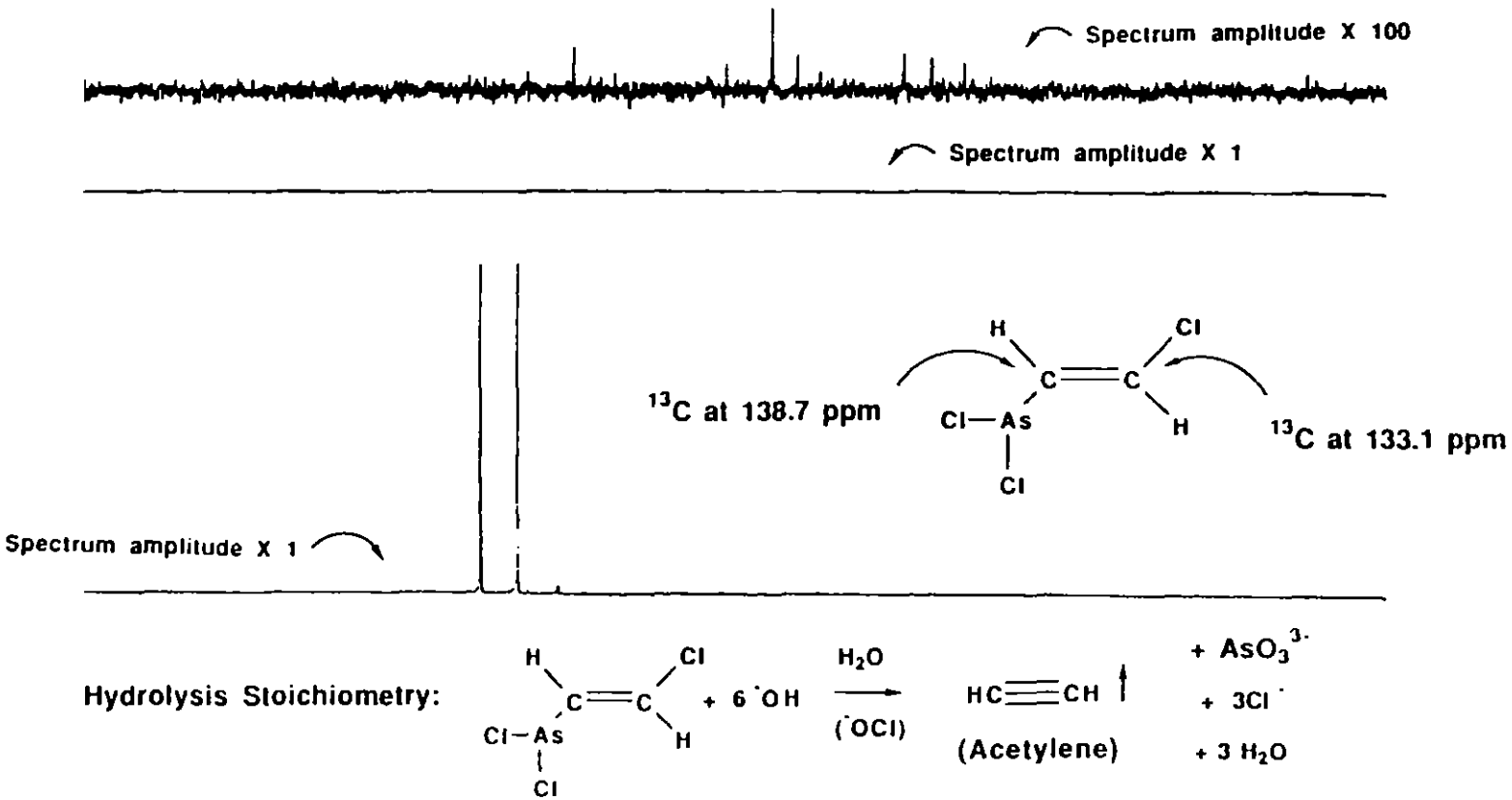
Lower Trace: Lewisite Starting Material (X 1)



Hydrolysis Stoichiometry:



8.1.17 Lewisite Hydrolysis in 5.25% NaOCl



8.1.18 Lewisite Hydrolysis in 10% Na_2CO_3

Experimental Conditions: 0.02 mL of Lewisite in 0.2 mL isopropanol plus 1.0 mL of 10% Na_2CO_3 : Sample miscible; a lot of gas (e.g., acetylene) evolved. Major peak at δ167.3 may be acetylene in solution; there are trace unknown peaks at δ161.7, 144.7, 132.6 (spectrum amplitude increased X10 to show these trace peaks).

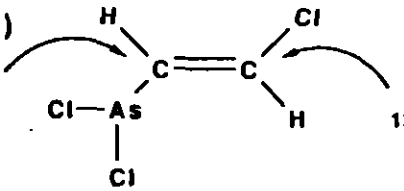
Results: Spectrum at 10 min shows: No Lewisite present; ^{13}C signal due to solvent. Sample appears to have reacted to give acetylene (gas) in solution.

Upper Trace: Hydrolysis Product (X 10)
Middle Trace: Hydrolysis Product (X 1)

No Lewisite carbons, peaks due to solvent (isopropanol).

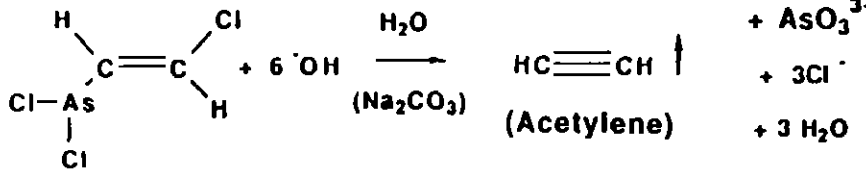
Lower Trace: Lewisite Starting Material (X 1)

^{13}C at 138.7 ppm

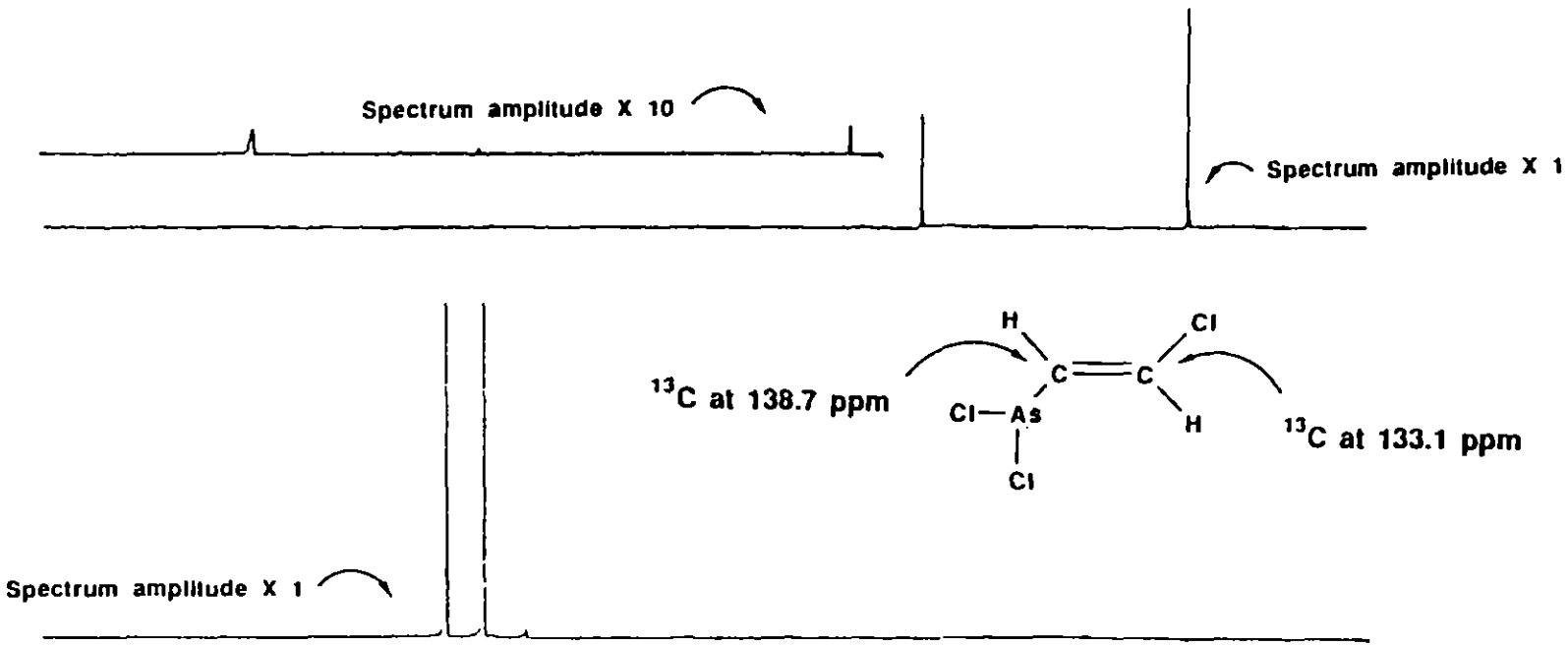


^{13}C at 133.1 ppm

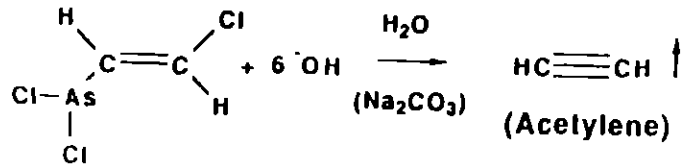
Hydrolysis Stoichiometry:



8.1.18 Lewisite Hydrolysis in 10% Na_2CO_3



Hydrolysis Stoichiometry:



BLANK PAGE

APPENDIX

8.2 Toxicological Data

8.2.1 Environmental Protection Agency
40 CFR Parts 160 and 792
FIFRA AND TSCA
GOOD LABORATORY PRACTICE STANDARDS

8.2.2 SUMMARY TOXICITY DATA ON
DECONTAMINATED CHEMICAL AGENTS

8.2.3 TYPE PROTOCOL 210880360000

8.2.4 CODE OF FEDERAL REGULATIONS
DEPARTMENT OF TRANSPORTATION
GUIDELINES FOR CLASSES OF POISONOUS MATERIALS

8.2.1 Environmental Protection Agency
40 CFR Parts 160 and 792
FIFRA AND TSCA
GOOD LABORATORY PRACTICE STANDARDS

Federal Register

Monday
December 28, 1987

Part III

Environmental Protection Agency

40 CFR Parts 160 and 792

Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and Toxic Substances Control Act (TSCA); Good Laboratory Practice Standards; Proposed Rules

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 160

[OPP-300165; FRL 3245-5]

Federal Insecticide, Fungicide and Rodenticide Act (FIFRA); Good Laboratory Practice Standards

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: EPA is proposing to expand the scope of the FIFRA Good Laboratory Practice (GLP) Standards by requiring GLP compliance for testing conducted in the field and for such disciplines of testing as ecological effects, chemical fate, residue chemistry, and, as required by 40 CFR 158.160, product performance (efficacy testing). EPA is proposing this amendment in order to ensure the quality and integrity of all data submitted to the Agency in conjunction with pesticide product registration, or other marketing and research permits. EPA is also proposing to amend the FIFRA GLPs to incorporate many of the changes made by the Food and Drug Administration (FDA) to its GLP regulations.

DATE: Submit written comments on or before March 28, 1988.

ADDRESS: Submit written comments, identified by the document control number (OPP-300165), by mail to: Information Services Section, Program Management and Support Division (TS-757C), Office of Pesticide Programs, Environmental Protection Agency, 401 M St. SW., Washington, DC 20460. In person, deliver comments to: Rm. 236, CM – 2, 1921 Jefferson Davis Highway, Arlington, VA.

Information submitted in any comment concerning this proposed rule may be claimed confidential by marking any part or all of that information as "Confidential Business Information" (CBI). Information so marked will not be disclosed except in accordance with procedures set forth in 40 CFR Part 2. A copy of the comment that does not contain CBI must be submitted for inclusion in the public record. Information not marked confidential may be disclosed publicly by EPA without prior notice to the submitter. All written comments will be available for public inspection in Rm. 236 at the address given above, from 8 a.m. to 4 p.m., Monday through Friday, excluding legal holidays.

FOR FURTHER INFORMATION CONTACT: Daniel A. Helfgott, Office of Compliance Monitoring (EN-342), Rm. E-707B, 401 M St. SW., Washington, DC 20460. Telephone: (202) 382-7825.

SUPPLEMENTARY INFORMATION: Following is an index to the remainder of this preamble:

I. Introduction

A. Legal Authority

These standards are promulgated under the authority of sections 3, 5, 6, 8, 18, 24(c), and 25(a) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), 7 U.S.C. 136 et seq., sections 408, 409, and 701 of the Federal Food, Drug, and Cosmetic Act (FFDCA), 21 U.S.C. 301 et seq., and Reorganization Plan No. 3 of 1970.

B. Background

EPA originally published enforceable FIFRA Good Laboratory Practice Standards in the Federal Register of November 29, 1983 (48 FR 53448), which were codified as 40 CFR Part 160. At the same time, EPA published GLP standards applicable to testing required under the Toxic Substances Control Act (TSCA, 48 FR 53922, 40 CFR Part 792). These regulations were promulgated in response to investigations by EPA and FDA during the mid-1970s which revealed that some studies submitted to the Agencies had not been conducted in accordance with acceptable laboratory practices. Some studies had been conducted so poorly that the resulting data could not be relied upon in EPA's regulatory decision-making process. For instance, some studies had been submitted which did not adhere to specified protocols, were conducted by underqualified personnel and supervisors, or were not adequately monitored by study sponsors. In some cases results were selectively reported, underreported, or fraudulently reported. In addition, it was discovered that some testing facilities displayed poor animal care procedures and inadequate record-keeping techniques. The FIFRA GLP standards specify minimum practices and procedures which must be followed in order to ensure the quality and integrity of data submitted to EPA in support of a research or marketing permit for a pesticide product.

When EPA published its final FIFRA and TSCA GLP standards in the Federal Register of November 29, 1983, the Agency sought to harmonize the requirements and language with those regulations promulgated by the FDA in the Federal Register of December 22, 1978 (43 FR 60013), and codified as 21 CFR Part 58. Differences between the two Agencies' current GLP regulations exist only to the extent necessary to reflect the Agencies' different statutory TSCA, FIFRA, and the Federal Food, Drug, and Cosmetic Act (FFDCA) responsibilities. Similar to the FDA GLP regulations, the FIFRA and TSCA GLPs delineate standards for studies designed to determine the health effects of a test substance; however, the TSCA GLPs also contain provisions related to environmental testing (i.e., ecological effects and chemical fate).

Compliance with EPA's GLP regulations has been monitored through a program of laboratory inspections and study audits coordinated between EPA and FDA. Under an Interagency Agreement originating in 1978, FDA carries out inspections at laboratories which conduct health effects testing. EPA primarily performs laboratory inspections and data audits for environmental studies.

After a thorough review of its GLP regulations and compliance program, FDA concluded that some of the provisions of the GLPs needed to be clarified, amended, or deleted in order to reduce the regulatory burden on testing facilities. Accordingly, FDA proposed revisions to its GLPs in the Federal Register of October 24, 1984 (49 FR 43530), which were intended to simplify the regulation without compromising study integrity. FDA's proposed revision has recently been published as a final rule in the Federal Register of September 4, 1987 (52 FR 33768).

EPA agrees with FDA that many provisions of the GLP regulations can be streamlined without compromising the goals of the GLPs. Therefore, EPA is proposing to amend the FIFRA GLP standards to incorporate many of the changes recently made by FDA to its GLP regulations. In addition, EPA is proposing to expand the scope of the FIFRA GLPs to include the environmental testing provisions currently found in the TSCA GLPs. EPA's proposed revision to the GLPs also extends the scope of the regulation to include product performance data (efficacy testing) as required by 40 CFR 158.160. In sum, the proposed FIFRA GLPs will allow the Agency to ensure the quality and integrity of all data

submitted in support of pesticide product research or marketing permits. In another notice in this Federal Register, EPA is proposing similar changes to the TSCA GLP standards.

C. Consistency With FDA GLP Regulations

It is EPA's policy to minimize the regulatory burden on the public which might arise from conflicting requirements which could be promulgated under different regulatory authorities. In keeping with this policy, the final FIFRA 1983 GLP standards, 40 CFR Part 160, followed the format and, with few exceptions, the wording of FDA's final GLP regulations, 21 CFR Part 58. Differences between the EPA and FDA GLP regulations were based upon varying needs and responsibilities under each Agency's regulatory statutes. This proposed revision to the FIFRA GLPs follows this same policy by conforming to many of the changes FDA made to its GLP regulations, published in the Federal Register of September 4, 1987 (52 FR 33768). EPA has varied from FDA's revised GLP regulations only when necessary due to EPA's statutory responsibilities. The most significant differences between the EPA proposal and the FDA revised GLP regulations are the scope of the testing and test systems affected.

More specifically, EPA is proposing to require compliance with the FIFRA GLPs for all studies submitted to the Agency which are intended to support pesticide product research or marketing permits. Under the current FIFRA Good Laboratory Practice regulations, and consistent with the FDA GLP regulations, this Agency only requires GLP compliance for health effects testing. However, unlike FDA, testing required by EPA in support of research or marketing permits may include ecological effects, environmental and chemical fate, and efficacy (as stipulated by 40 CFR 158.160 *Product performance data requirements*), as well as health effects testing. Therefore, in an effort to attain consistency in the quality and the integrity of all data submitted to the Agency, EPA has determined that it is necessary to expand the scope of the FIFRA GLPs to require that all types of testing which are used to obtain data in support of research or marketing permits be conducted in accordance with the proposed GLP standards.

EPA's proposed FIFRA GLP standards also vary from FDA's in their coverage of testing conducted in the field. To ensure the quality and integrity of all data submitted in support of research or marketing permits, EPA believes that GLP standards must apply whenever data collection occurs. Because many of the test data required by EPA are developed in the field, or more accurately in outdoor laboratories (i.e., ground-water studies, air monitoring studies, degradation in soil, etc.), EPA is proposing to include field testing within the scope of these regulations.

This Agency's proposed FIFRA GLPs also differ from FDA's in the scope of the requirements provided for test system care facilities, test system supply facilities, and test system care. Because testing required by FDA is focused on health testing, in which animals are the central test system, it is appropriate for FDA's GLP regulations to focus on requirements for appropriate animal care facilities (21 CFR 58.43), adequate animal supply facilities (21 CFR 58.45), and proper animal care (21 CFR 58.90). However, the broad range of testing required by EPA may involve plants, soils, and microorganisms, as well as animals, for the primary test systems. In order to ensure the quality and integrity of all data submitted to this Agency, it is proposed that § 160.43 *Animal care facilities*, § 160.45 *Animal supply facilities*, and § 160.90 *Animal care* be expanded to cover facilities, handling, and care of all test systems. Accordingly, EPA is proposing that these sections be retitled as follows: § 160.43 *Test system care facilities*, § 160.45 *Test system supply facilities*, and § 160.90 *Animal and other test system care*. Further, in most instances, EPA is proposing to replace the term "animal," which is currently used in the FIFRA GLP regulations, with the broader term "test system." Specifically, this change is proposed in §§ 160.43, 160.45, 160.81, 160.90 and 160.120. These proposed changes are further discussed in Unit I.D. of this preamble.

The remaining differences between the EPA and FDA GLP regulations are described in the preamble to this proposed rule and the preamble to the FIFRA Good Laboratory Practice Standards, published in the Federal Register of November 29, 1983 (48 FR 53946). EPA has coordinated this proposal with FDA and has considered comments received on the proposal to amend the FDA GLP regulations (49 FR 43530; October 29, 1984).

D. Proposed Changes to the GLP FIFRA Regulations

1. *Section 160.3 Definitions*. a. EPA proposes to define the term "carrier" to mean any material, such as feed, water, soil, nutrient material, etc., with which the test substance is combined for administration to test organisms. The term "carrier" is currently used in § 160.113 and is not defined. EPA proposes to define this term to clarify it.

b. EPA proposes to conform with the September 4, 1987, FDA GLP regulations by amending the definition of "control substance" to exclude feed and water. EPA agrees with FDA's statement regarding this change (52 FR 33769; September 4, 1987) that "the term control [substance] should be reserved for the discrete substances/articles, and vehicles other than water administered to groups of the test system to provide a basis of comparison with the test [substance]."

FDA contends that, under the current definition of "control substance," because the control group of a test system provides the basis for comparison with a test substance, any substance administered to the control group would be considered a control substance. This would mean that feed and water given to the control group of a study are considered a control substance. For instance, in studies in which the test substance or mixture is administered to the test system orally, through feed or drinking water, gavage, or injection, the feed or water is considered a control substance. As a control substance, the feed or water is subject to § 160.105(a) for substance characterization, § 160.105(b) for testing for stability and solubility, § 160.105(c) for requirements for appropriate storage, § 160.105(d) for retention of reserve samples, and § 160.107 for documentation of receipt and distribution of each batch. EPA agrees with FDA that placing these requirements on the use of feed and water as a control substance in control groups unnecessarily burdens the regulated community and is not essential for ensuring the quality and integrity of the data generated by a study.

However, under 40 CFR Part 160, feed and water used as a carrier for the test and control substances or mixtures are still covered by the applicable sections for the testing and storage of test, control, and reference substances and mixtures. For example, § 160.31(e) requires testing facility management to ensure materials are available as scheduled; § 160.45 requires that test system supply facilities shall be provided to ensure proper feed storage; § 160.81(b)(2) requires Standard Operating Procedures (SOP) for test system care, including nutrition; § 160.90(g) requires periodic analysis of feed and water to ensure that contaminants which would interfere with the study are not present; § 160.120(a)(9) requires the protocol to

...scribe and/or identify the diet used in the study, including the level of contaminants expected in the dietary materials.

c. EPA also proposes to modify the definition of "control substance" by adding the phrase "for no effect levels." This addition to the definition is being proposed merely to clarify the difference between the term "reference substance" and "control substance." While a control substance is used to determine a baseline comparison to no effect levels, a reference substance is used to determine a baseline comparison to an established effect level.

d. EPA proposes to add and define the terms "experimental start date" and "experimental termination date." "Experimental start date" is proposed to mean the first date the test substance is applied to the test system. Under this definition, as of the experimental start date: (1) Under proposed § 160.105(b), the stability and, if important to the conduct of the experiment, the solubility of the test, control, and reference substances would have been determined; (2) under proposed § 160.113(a)(2), the stability and, if important to the conduct of the experiment, the solubility of the test, control, and reference substance in the mixture would have been determined and; (3) under proposed § 160.120(a)(4), the proposed experimental start date would appear in the protocol.

EPA proposes that "experimental termination date" be defined as the last date on which data are collected directly from the study. Under § 160.120(a)(4) as proposed, EPA would require the proposed experimental termination date to appear in the protocol. EPA considers histopathology after scheduled terminal animal sacrifice to be carried out before the experimental termination date.

Experimental start and termination dates would be expressed as the actual calendar dates, not just time-line increments. Therefore, when determining the proposed experimental start and termination dates, as would be required by proposed § 160.120(a)(4), the submitter should consider any lag time relating to protocol approval and laboratory contracting.

e. EPA proposes to add and define the term "reference substance" to mean any chemical substance or mixture or material other than a test substance that is administered to or used in analyzing the test system in the course of a study for purposes of establishing a basis for comparison with the test substance for known effect levels. EPA proposes the use of the term "reference substance" in the revised FIFRA GLP regulations because of its common usage in environmental testing and, therefore, its proposed use in these regulations.

In this proposed GLP regulation, all the requirements provided for test and control substances would also apply to "reference substances." Accordingly, the term "reference substance" has been added wherever the term "test and control substance" appears in these standards. Specifically, the term "reference substance" is added to proposed § 160.29 (d) through (f); § 160.43(b); § 160.47(a) (1) through (3) and (b); § 160.81(b)(3); the Subpart F heading; § 160.90(c); § 160.105 (a) through (e); § 160.107; § 160.113 (a) and (b); § 160.120(a) (2), (9), and (11); § 160.185(a) (4) and (5); and § 160.195(c).

f. EPA proposes to broaden the definition of the term "study" to be consistent with EPA's proposal to amend these regulations to require GLP compliance for all testing required to be submitted to the Agency in conjunction with a pesticide product's research or marketing permit.

EPA is proposing to delete the phrase "in vivo or in vitro" from the definition of "study." The Agency still intends the requirements of these regulations to apply to "in vivo and in vitro" experiments. However, since the Agency intends these regulations to apply to all studies required to be submitted under FIFRA, including those conducted in the field, EPA feels that including the phrase "in vivo or in vitro" in the definition of "study" is too limiting.

Further, EPA is proposing to delete the term "prospectively" from the definition of "study." In this way, epidemiological studies, which could be "retrospective," will be required to be presented to the Agency in accordance with the GLP standards. EPA recognizes that data used in an epidemiological study may not have been generated in conformance with the FIFRA GLP standards, however, it is EPA's contention that the epidemiological study itself can be conducted and submitted to the Agency in accordance with the GLPs.

EPA is also proposing to delete from the current definition of "study" the following sentence: "The term does not include studies utilizing human subjects or clinical studies or field trials in animals." Again, this change is consistent with EPA's intention to require compliance with GLPs for all studies submitted to the Agency in support of a research or marketing permit for pesticide products, including biomonitoring or efficacy studies. FIFRA does not prohibit pesticide testing on humans (as long as the informed-consent conditions specified in FIFRA section 12(a)(2)(P) are met, and provided the records required by 40 CFR 169.2(j) are maintained). EPA feels that testing that is performed on humans must be conducted in accordance with the GLPs, if that data is submitted to the Agency in support of a marketing or research permit.

It is also proposed that studies designed to determine the physical or chemical characteristics of a test substance be included within the scope of these regulations. Therefore, EPA is proposing that the phrase "or to determine physical or chemical characteristics of a test substance" be deleted from the definition of the term "study." This proposed change is consistent with the definition of the term "study" as it now appears, and as it is proposed to appear, in the TSCA Good Laboratory Practice Standards at 40 CFR Part 792. However, as specified in proposed § 160.135, exclusions from certain GLP requirements are provided for studies related to determining the physical or chemical characterization of a test, control, or reference substance (e.g., studies designed to determine color, odor, physical state, melting point, pH measurement, etc.).

g. EPA proposes to incorporate the FDA definitions for "study completion date" and "study initiation date" in § 160.3. "Study completion date" is proposed to mean the date the final report is signed by the study director. EPA advises that the phrase "close of the study" as used in § 160.33(f), and the phrase "study is completed" as used in § 160.195(b)(3) both refer to the "study completion date." Consistent with this definition, as of that date: (1) Under § 160.33(f), the study director must ensure that all raw data, documentation, protocols, specimens, and final reports are transferred to the archives; (2) after this date under § 160.185(c), corrections or additions to the final report must be in the form of an amendment by the study director under the procedures specified in that section; and (3) in the applicable situations described in § 160.195(b)(3), records must be maintained for a period of at least 2 years following the study completion date.

EPA proposes to define "study initiation date" as the date the protocol is signed by the study director. EPA advises that the phrase "study is initiated" as used in § 160.31(a), and the phrase "study was initiated" as used in § 160.35(b)(1) would refer to the "study initiation date." Therefore, as of the study initiation date: (1) Under § 160.31(a), the testing facility management would designate a study

director: (2) under § 160.35(b)(1), the study would be entered on the master schedule sheet by the quality assurance unit; and (3) under § 160.120(b), after this date all changes or revisions in the protocol would be documented, signed by the study director, and dated. EPA also expects that as of the study initiation date, under § 160.31(e), the testing facility management would have ensured that personnel, resources, facilities, equipment, material, and methodologies are available as scheduled.

h. EPA proposes to replace the term "test substance or mixture" with the term "test substance." This is an editorial change which makes usage consistent in the GLP standards. The term "test substance" is proposed to be defined to include mixtures.

i. EPA proposes to expand the definition of "test system" to include chemical or physical matrices (e.g., soil or water). This proposal is consistent with the Agency's intent to expand these regulations to include environmental effects testing.

j. EPA proposes to define the term "vehicle" to mean any agent which facilitates the mixture, dispersion, or solubilization of a test substance with a carrier.

2. *Section 160.31 Testing facility management.* In conformance with the revised FDA GLP regulations, in § 160.31(b), EPA proposes to delete the requirement that the replacement of a study director must be documented as "raw data." EPA agrees with FDA that this requirement is redundant with other provisions of the GLPs. For instance, § 160.35(b)(1) states that the master schedule sheet must contain the name of the study director. As FDA notes (52 FR 33770), any replacement of the study director would be reflected on the master schedule sheet, which is already considered "raw data." Further, § 160.120(b) states that all changes in an approved protocol must be documented and signed by the study director. Replacement of the study director is considered to be a change in the approved protocol.

3. *Section 160.35 Quality assurance unit (QAU).* a. In § 160.35(a), EPA proposes to conform with the revised FDA GLP regulations by substituting the term "which" for the current phrase "composed of one or more individuals who." This change clarifies that EPA does not require the QAU to be a fixed, permanently staffed unit whose only functions are to monitor the quality of a study. The Agency is only concerned that there be a distinct separation of duties between those personnel involved with the conduct or direction of a study and those personnel performing quality assurance on the same study. Therefore, EPA does intend proposed § 160.35(a) to prohibit personnel from performing quality assurance activities on their own study.

b. In § 160.35(b)(1), EPA proposes to delete the requirement that the name of the study sponsor appear on the master schedule sheet. Instead, it is proposed that under § 160.35(b)(1) the sponsor's identity appear on the master schedule sheet. This change is being proposed to be consistent with the FDA's recent revision and to provide the regulated community the option of using an identity code on the master schedule in lieu of the sponsor's name.

EPA agrees with FDA's contention that requiring the sponsor to be identified specifically by name on the master schedule is not essential to fulfill the requirements of the GLPs or the goal of ensuring the quality and integrity of the data generated from the studies. However, while the name of the study sponsor would not be required to appear on the master schedule sheet, this information must be made available to the Agency upon request.

c. As in the revised FDA GLP regulations, EPA is also proposing to delete the requirement in § 160.35(b)(1) that the master schedule sheet contain the status of the final report. EPA agrees with FDA that this requirement is redundant in view of the other information required by § 160.35(b)(1) such as the date the experiment began and the current status of each study.

d. In conformance with the revised FDA GLP regulations, EPA proposes to modify the requirements of § 160.35(b)(3) to provide for inspections of a study on a schedule adequate to ensure the integrity of the study. This section currently specifies that the quality assurance unit must inspect each phase of a study periodically. This section also currently specifies that for studies lasting more than 6 months, quality assurance inspections shall be conducted every 3 months, and for studies lasting less than 6 months, quality assurance inspections shall be conducted at intervals adequate to ensure the integrity of the study.

The proposed changes to this section will allow the QAU the necessary latitude to adjust its monitoring activities to meet the individual problems of each study. EPA agrees with FDA's contention that an inspection of each phase of the study is not necessary to ensure that a study is being conducted properly. However, EPA also agrees with FDA that each study, no matter how short, must be inspected at least once while in progress. EPA expects that by allowing the QAU flexibility in designing a reasonable inspection schedule, the goal of ensuring the quality of the study can be best achieved.

e. Consistent with the revised FDA GLPs, EPA is proposing to delete § 160.35(e) in its entirety. Section 160.35(e) currently requires that all quality assurance records be kept in one location at the testing facility. As FDA pointed out in its October 29, 1984, proposed GLP revision, since § 160.190(b) already requires the use of archives for the orderly storage and expedient retrieval of all reports and records, the requirements of § 160.35(e) are not necessary. However, EPA maintains that all reports and records, including those of the QAU, must be easily accessible and made available to EPA and FDA inspectors when requested.

4. *Section 160.41 General.* FDA has deleted from its GLPs the requirement that the location of each testing facility be suitable to facilitate the proper conduct of studies. However, EPA is proposing that § 160.41 require that testing facilities which are not located within an indoor controlled environment be suitably located to facilitate the proper conduct of studies.

The studies FDA requires are generally conducted within the confines of a traditional indoor laboratory. Because the conditions specified within a protocol can be artificially manipulated within the traditional indoor laboratory, the location of these laboratories is generally not a factor in determining the quality of a study. Therefore, it is not necessary to ensure that a traditional indoor testing facility is suitably located to facilitate the proper conduct of the study.

However, the studies EPA requires are not necessarily conducted within the confines of the traditional indoor scientific laboratory (i.e., field studies, groundwater studies, ecological toxicity studies, etc.). EPA considers any site where testing is undertaken to generate data required by the Agency to be a testing facility. The conditions required by the protocol are not necessarily conducive to artificial manipulation in the field, or other outdoor testing facilities. Therefore, ensuring the suitability of the location of these types of testing facilities is both a valid and necessary part of EPA's GLP Standards.

5. *Section 160.43 Test system care facilities.* a. EPA is proposing to revise the title of § 160.43 from "Animal care facilities" to "Test system care facilities". The proposed heading for § 160.43 more adequately reflects the

Agency's intent to specify facility requirements for the care of chemical or physical matrices (e.g., soil or water), plants, and microorganisms, as well as animals. Accordingly, the Agency is proposing to further modify § 160.43 by incorporating the term "test system" when facility requirements should extend beyond "animal" care.

Consistent with the Agency's intent stated above, paragraphs (a)(1), (a)(2), (d), (e), (f), (g), and (h) in proposed § 160.43 have been added or modified in order to ensure proper care facilities are provided for the additional test systems covered by the expanded section.

b. EPA proposes to modify § 160.43(a) to allow testing facilities to provide for isolation areas rather than quarantine areas. This change is consistent with the proposal to modify § 160.90(b) to allow "isolation" of newly received animals rather than require "quarantine" [See Unit I.D. of this preamble for a discussion of proposed § 160.90(b)].

c. In § 160.43(c), EPA proposes to delete the requirement that separate areas be provided in all cases for the diagnosis, treatment, and control of test system diseases. Instead, it is proposed that such separate areas be provided "as appropriate." This proposal is consistent with the September 4, 1987, revised FDA GLP regulations.

EPA has proposed this modification in order to allow laboratories the option of disposing of diseased animals and other test systems without also bearing the expense of maintaining separate areas in testing facilities for diagnosis, treatment, and control of disease. Additionally, EPA recognizes that the diagnosis and treatment requirements of § 160.43(c) may not be appropriate when dealing with such test systems as soil, plants, or microorganisms. However, if the decision is made not to dispose of the test system, then test system care facilities, as specified in proposed § 160.43(c), must be provided.

d. EPA proposes to conform to the revised FDA GLPs by deleting § 160.43(e) in its entirety. Currently, § 160.43(e) requires test system facilities to be designed, constructed, and located so as to minimize disturbances which may interfere with the study. EPA agrees with FDA that this provision is already adequately covered in § 160.41, which requires that facilities be of suitable size, construction, and, for outdoor testing facilities, location to facilitate the proper conduct of the study.

6. *Section 160.45 Test system supply facilities.* a. EPA proposes to expand the scope of § 160.45 to require that supply facilities necessary for environmental testing be provided when appropriate.

b. Consistent with the proposed expanded scope of this section, EPA is also proposing to retitle § 160.45, from "Animal supply facilities" to "Test system supply facilities."

c. EPA also proposes to modify § 160.45 to state "Perishable supplies shall be preserved by appropriate means." This change is being proposed to conform with the revised FDA GLPs and recognizes that there are a variety of acceptable storage and preservation procedures available besides refrigeration. Depending on the stability characteristics of the perishable material, acceptable storage and preservation methods may include desiccation, room temperature-low humidity, and constant temperature-low humidity.

d. EPA also proposes to delete the phrase "or feed" from the last sentence of § 160.45. Both EPA and FDA consider "feed" to be a "supply." Therefore, the use of the word "feed" in § 160.45 is redundant.

7. *Section 160.49 Laboratory operation areas.* a. EPA proposes to conform with FDA's revised GLP regulations by deleting paragraph (b) from § 160.49, adding the phrase "and specialized" after the word "routine" and before the word "procedures," and deleting the qualifying phrase "including specialized areas for performing activities such as aseptic surgery, intensive care, necropsy, histology, radiography, and handling of biohazardous materials."

Paragraphs (a) and (b), as currently worded, describe activities which require that separate laboratory space be provided. As FDA noted in its proposal to modify its corresponding section (49 FR 43532), the list of activities that currently appears in paragraphs (a) and (b) is not all inclusive and is not essential for the clarity of these sections. Further, by adding the phrase "and specialized," the proposed new paragraph will encompass all activities now listed in paragraphs (a) and (b).

b. In § 160.49, EPA proposes to add the phrase "and other space" after the words "laboratory space" and before the word "shall." As discussed in Unit I.C. of this preamble, this change to § 160.49 is being proposed to reflect that testing does not necessarily take place within the confines of a traditional indoor laboratory. Proposed § 160.49 would require that there be enough space provided to perform the procedures required by the protocol wherever testing takes place (i.e., indoor laboratory or field station).

8. *Section 160.53 Administrative and personnel facilities.* As in the revised FDA GLP regulations, EPA proposes to delete § 160.53 in its entirety. EPA agrees with FDA that the requirements of this section are not necessary for achieving the goals of the FIFRA GLP standards.

9. *Section 160.61 Equipment design.* In § 160.61, EPA proposes to delete the phrase "Automatic, mechanical, or electronic" from the beginning of the first sentence. EPA agrees with FDA that the deletion of these qualifying terms provides for a more general interpretation of the word "equipment."

10. *Section 160.63 Maintenance and calibration of equipment.* a. Consistent with the FDA GLPs, EPA is proposing to amend § 160.63(b) to state that standard operating procedures (SOPs) for remedial action for equipment, in the event of failure or malfunction of equipment, need only be established when "appropriate." This change acknowledges that laboratories may choose to discard rather than repair equipment, and in such cases SOPs which delineate remedial action are not necessary.

b. EPA is also proposing to conform to the revised FDA GLP regulations by deleting from § 160.63(b) the provision that copies of the SOPs shall be made available to laboratory personnel. EPA still believes that laboratory personnel must have access to laboratory SOPs; however, since this requirement is clearly stated in § 160.81(c), EPA considers the inclusion of this requirement in § 160.63(b) to be redundant.

11. *Section 160.81 Standard operating procedures.* a. In § 160.81(b) (1), (2), (6), (7), and (12), EPA is proposing to replace the term "animal" with the term "test system." As discussed previously in this preamble, this modification is consistent with the broad scope of test systems which may be used in testing undertaken in support of a pesticide product research or marketing permit.

b. In § 160.81(b)(5), EPA is proposing to require that SOPs be established for tests wherever the testing is undertaken, including those conducted in the field. Accordingly, it is proposed that § 160.81(b)(5) read "Laboratory or other tests" (see discussion of "field testing" in Unit I.C. of this preamble).

c. In conformance with FDA's revised GLP regulations, EPA is proposing to delete the list of examples for laboratory manuals and SOPs required to be made immediately available under § 160.81(c). EPA still intends that laboratory areas must have immediately available manuals and SOPs for laboratory procedures being performed. This requirement still includes toxicology, histology, clinical chemistry,

hematology, teratology, and necropsy, if applicable. However, this list is not all inclusive and is too broad to serve as a useful guide. For example, this requirement also includes SOPs for the maintenance, repair, and calibration of equipment as described in § 160.63(b).

d. EPA is also proposing to amend the language of § 160.81(c) to clarify that the requirement of this section also applies to field testing facilities. Therefore, it is proposed that § 160.81(c) will read, "Each laboratory *or other study* area shall have immediately available manuals and standard operating procedures relative to the laboratory or field procedures being performed."

12. *Section 160.90 Animal and other test system care.* a. EPA is proposing to retitle § 160.90 from "Animal care" to "Animal and other test system care". As previously stated, testing required by EPA may involve plants, soils, microorganisms, and other test systems, in addition to animals. The proposed title to § 160.90 reflects the broader scope of this Agency's regulatory responsibilities, these regulations, and this section, to provide for the quality and integrity of all data submitted in support of pesticide product research and marketing permits.

Consistent with the Agency's proposal stated above, paragraphs (b), (d), (e)(1), (f), (g), and (j) in proposed § 160.90 have been added or modified in order to ensure the proper care of all test systems used in a study.

b. EPA proposes to modify § 160.90(b) to provide for the evaluation of a test system's health status, or the appropriateness of the test system for the study, according to acceptable "scientific practice." This section, as proposed, will still require that newly received animals must have their health status evaluated according to acceptable veterinary medical practices. However, EPA recognizes that it may not be appropriate to evaluate the health status of certain test systems (e.g., soil or water) or to require that a plant, microorganism, soil, or water be evaluated according to acceptable veterinary medical practice to determine their appropriateness for a study. EPA is only concerned that test systems used in a study are free of any disease or condition which may interfere with the purpose or conduct of the study, and that the proper precautions, as stated in § 160.90(b), are taken to comply with this requirement.

c. Additionally, EPA is proposing to modify § 160.90(b), to require "isolation" rather than "quarantine" of newly received animals. This proposal is consistent with FDA's revision to its GLPs.

As previously stated, the intent of § 160.90(b) is to prevent the entry of unhealthy or inappropriate test systems into the study, as required by § 160.90(c). Currently, § 160.90(b) provides that this intent be achieved through "quarantine." However, the term "quarantine" suggests a rigid set of procedures, including a mandatory holding period, a specific list of diagnostic procedures, and the use of specialized facilities and test system care practices, which may be an unnecessary burden to industry.

EPA agrees with FDA's conclusion, discussed in the preamble to its revised GLPs (52 FR 33775; September 4, 1987), that isolation and evaluation of health status are sufficient precautions against contamination of test systems and, therefore, fulfill the intent of this section. FDA further states that such a revision would provide laboratories the flexibility to develop isolation and health status evaluation procedures best suited for the age, species, class, and type of the test system, as well as the type of study to be performed.

d. EPA proposes to conform to the FDA GLPs by modifying § 160.90(c) to require isolation of diseased test systems only when necessary.

Currently, § 160.90(c) requires that animals which contract a disease or condition shall be isolated in all cases. This requirement would in turn require that separate facilities be available for the isolation of these animals. However, as discussed in the proposal for § 160.43(c), both EPA and FDA believe that laboratories should be given flexibility in their disposition of diseased test systems. As FDA discussed in the proposed revisions to its GLP regulations (49 FR 43533; October 29, 1984), the proposed modification to § 160.90(c) will allow laboratories the option of: (1) Leaving the diseased test system in the experiment provided that the integrity of the study will not be adversely affected by this action; (2) disposing of the test system; or (3) isolating treating, and returning the test system to the study.

13. *Section 160.105 Test, control, and reference substance characterization.* a. In revised 21 CFR 58.105(a), FDA deleted the requirement that test and control substance characteristics shall be determined and documented for each batch "before the initiation of the study." This change has not been adopted by EPA in its proposed revision to § 160.105(a). However, EPA proposes to modify § 160.105(a) to require that test, control, *or reference* substance characterization be determined and documented for each batch before its use in the experiment. EPA feels that this proposed requirement is necessary because it is essential that characteristics of test, control, and reference substances be known prior to their administration or use in an experiment.

EPA's recent experience with antimony trioxide has shown that extensive analytical work was necessary prior to test initiation. Certain assumptions regarding the product's characteristics were used in the protocols for antimony trioxide testing which proved invalid. These invalid assumptions necessitated modifications to the proposed study, resulting in the delay and rescheduling of other subsequent studies. If the analytical work had preceded the toxicology studies, the studies would not have failed and modifications to the studies would not have been necessary. The Agency's conclusion is that it is better to delay study schedules than to initiate improper experimental procedures which will produce invalid results.

b. FDA has modified 21 CFR 58.105(b) to provide for the determination of the stability of the test or control substance either before the initiation of the study or through periodic analysis of each batch according to written standard operating procedures. EPA has chosen not to adopt this approach in proposed § 160.105(b) because the Agency does not agree that stability can adequately be demonstrated by periodic analysis without initial evaluation.

Further, there are many studies required by EPA where solubility of the test, control, or reference substance is of critical importance, such as aquatic toxicity studies. Therefore, EPA is proposing that solubility of the test, control, or reference substance be determined before the experimental start date if knowledge of solubility characteristics is relevant for the proper conduct of the experiment.

It is EPA's contention that both stability and solubility of the test, control, and reference substance need to be determined before the experimental start date in order to ensure proper handling and administration of the test substance to the test system. However, since the determination of the solubility of the test, control, and reference substance is not a requirement in FDA's GLP regulations, EPA is interested in receiving public comment on this issue.

14. *Section 160.113 Mixtures of substances with carriers.* a. FDA has revised 21 CFR 58.113(a)(2) to require determination of the stability of the test and control substance in a mixture as required by the conditions of the study, either before the initiation of the study

or through periodic analysis of each batch. While EPA does not propose to modify § 160.113(a)(2) to provide the option of determining the stability of the mixture either before study initiation or through periodic analysis (see discussion for § 160.105(b)), EPA will modify this section to require stability testing only to the extent required by the conditions of the experiment. As proposed for § 160.105(b), EPA is also proposing to require that when appropriate to the conduct of the experiment, solubility of the test, control, or reference substance in the mixture be determined in the same manner (see discussion for § 160.105(b)). Additionally, as proposed for § 160.105 (a) and (b), EPA is proposing to replace the phrase "before the initiation of the study" with the phrase "before the experimental start date" (see discussion for § 160.105(a)).

The phrase "as required by the conditions of the experiment" has been added in order to clarify that determination of stability and, if appropriate, solubility of a test, control, or reference substance in a mixture is only necessary to support the actual time of use in the experiment. Therefore, it is not necessary to provide data which illustrate long-term stability of a mixture when the actual time that the mixture is used is short-term. For example, a test, control, or reference substance in a mixture that will be used the same day it is prepared will only require data sufficient to show stability and, if appropriate, solubility for 1 day.

b. EPA proposes to add § 160.113(c) which states, that if a vehicle is used to facilitate the mixing of a test substance with a carrier, assurance shall be provided that the vehicle does not interfere with the integrity of the test.

15. *Section 160.120 Protocol.* a. In revised 21 CFR 58.120(a), FDA has replaced the qualifying phrase "but shall not necessarily be limited to" with the phrase "as applicable." EPA proposes to adopt FDA's approach with some modifications. It is proposed that the phrase "Where applicable" appear before the information specified in § 160.120(a)(9), and continue to appear before the information required by § 160.120(a)(6). The phrase "but shall not necessarily be limited to" would remain in this section.

In FDA's discussion of this proposal (49 FR 43533; October 29, 1984), concerns were expressed that some of the information required to appear in the protocol is not applicable to all types of testing. Specifically, FDA points to the information required by 21 CFR 58.120(a) (9) and (11). In 21 CFR 58.120, paragraph (a)(9) requires a description of the diet used in a study as well as solvents, emulsifiers, and/or other materials used to solubilize or suspend the test or control substance before mixing with the carrier. FDA points out that this requirement is not applicable to radiation-emitting products. Section 58.120(a)(11) specifies that the protocol shall specify dosage level, and this requirement is not applicable to implantable medical devices.

Clearly, the basis for FDA's change is to accommodate concerns that are specific to the types of testing required by FDA and do not necessarily apply to testing required by EPA. Further, EPA is concerned that placing the phrase "as applicable" in § 160.120(a) suggests that there may be cases where it is not applicable for any of the other information required by § 160.120(a) to appear in the protocol. Therefore, the phrase "as applicable" should only appear before those items which are not necessarily appropriate to appear in the protocol for certain types of testing.

For example, there may be testing required by EPA where it may not be appropriate to require a protocol to contain the information specified in § 160.120(a)(9), such as describing and/or identifying the diet of a human subject involved in exposure testing. Therefore, EPA proposes to add the phrase "Where applicable" before the information specified in proposed § 160.120(a)(9).

b. In revised 21 CFR 58.120(a)(4), FDA has deleted the requirement that the protocol contain "The proposed starting and completion dates." EPA is proposing to retain this requirement in § 160.120(a)(4), but is proposing to modify this paragraph to require, "The proposed experimental start and termination dates."

EPA believes that this information is necessary for the evaluation of a protocol, and the Agency scheduling of additional related studies and audit reviews. Section 160.120(a)(4) is related to the selected study method, laboratory, and specialist availability, and other Agency and industry priorities. Often a group of experiments are carried out in sequence, so that both start and termination dates affect subsequent study expectations and timetables. Projected experimental start and termination dates identify the normal duration for a given experiment type and reflects any special considerations that may be unique to a laboratory, anticipated analytical or methodology work, and available resources, and it may also affect pending regulatory timetables.

Given that there are hundreds of studies that EPA must track, these estimated schedules, combined with those from other studies, allow the Agency to more efficiently schedule audits and regulatory action. Further considerations are the following: (1) The availability of composite schedules for many studies may be necessary to set realistic regulatory action goals; (2) composite study schedules are evaluated to schedule audits while several studies are ongoing or recently completed, and which may all be at a given laboratory or geographic location, thus directly reducing EPA resources necessary for audit and regulatory review functions; and (3) standard business management by objectives requires intermediate calendar goals when scheduling multiple outputs, or a long-term single product. The master on-site laboratory schedule will incorporate these dates to carry out the study.

c. In 21 CFR 58.120(a)(5), FDA has deleted the requirement that the protocol contain a justification for the selection of the test system. EPA has chosen to leave this requirement in proposed § 160.120(a)(5).

Environmental studies, including both ecological effects and chemical fate, are more diverse than health effects testing. Further, details relevant to the test system design are more chemically dependent in the case of environmental effects and chemical fate testing than in the case of health effects testing. Many of the test systems in environmental studies must be modified in accordance with specific chemical characteristics. Therefore, EPA must allow a much broader range of flexibility in the nature of tests and selection of test systems. In order to fully understand the test and its results, EPA needs to have a discussion of the reasons for selection of the test system. In addition, EPA recognizes that industry may be engaged in state-of-the-art environmental testing. Under proposed § 160.120(a)(5), EPA can keep abreast of industry advances in such testing and ensure that their use of test systems is appropriate. EPA is interested in receiving public comment on whether to limit the requirement that the protocol contain a justification of the test system to environmental testing.

d. FDA has deleted from 21 CFR 58.120(a)(10) the requirement that the protocol include the route of administration and the reason for its choice. EPA has chosen to retain this requirement in proposed § 160.120(a)(10).

The chemicals regulated by FDA will usually have a predefined route of exposure. Therefore, it makes sense for FDA to eliminate the requirement to stipulate the route of administration and

the reason for its choice within the protocol. Unlike FDA, EPA is concerned with presence in or exposure to various media (i.e., air, water, soil, sediment, chemicals, etc.) and may not know in advance the routes of exposure for the chemicals it regulates. Most chemicals and products regulated by EPA do not have set routes of exposure and may even have multiple routes of exposure. Therefore, EPA must consider a wide range of possible exposure routes in its regulatory decisions. Further, the route of administration is essential to determine the effectiveness of a test system for the purposes of a specific toxicology study. The route of administration affects the real dosage rates and, therefore, affects whether the impact of the exposure of the test substance is acute or chronic.

Therefore, EPA believes that, for its purposes, it is essential that the protocol contain the route of administration and the reason for its choice. This requirement will therefore remain in the FIFRA GLPs in § 160.120(a)(10).

e. EPA proposes to delete current § 160.120(a)(12) in its entirety. Currently, § 160.120(a)(12) requires that the protocol contain the method by which the degree of absorption of the test and control substance by the test system will be determined. EPA agrees with FDA's conclusion that this requirement is not necessary in the protocol.

f. In proposed § 160.120(a)(14), redesignated from current paragraph (a)(15), EPA proposes to conform with FDA's revised GLP regulations and require that the study director's signature be dated on the protocol.

EPA is proposing in § 160.3 that the study initiation date be defined as the date the protocol is signed by the study director. It is through the proposed requirement of § 160.120(a)(14), that the Agency will be able to identify the official study initiation date.

16. *Section 160.130 Conduct of a study.* a. FDA has modified 21 CFR 58.130(d) to provide that records of gross findings for a specimen from postmortem observations "should" be made available to the pathologist when examining that specimen's histopathology. EPA is proposing to retain the requirement that these records "shall," in all cases, be provided to a pathologist during study of the specimen.

EPA agrees with FDA's conclusion that for most studies it is important for the pathologist to have the records of gross findings available when examining a specimen histopathologically. However, it is FDA's contention that replacing the word "shall" with the word "should" will allow the histopathological evaluation of specimens in a "blind" fashion. EPA also recognizes that it may be appropriate for some studies to provide for "blinding" in histopathological evaluation. However, EPA maintains that, when specified by the protocol, the pathologist can accomplish "blinding" without violating § 160.130 by not looking at the records which have been provided. Therefore, it will remain EPA's requirement that the pathologist must have access to the records of gross findings when examining a specimen histopathologically.

b. In conformance with the revised FDA GLP regulations, in § 160.130(e), EPA proposes to replace the terms "computer" and "computer driven" with the term "automated data collection." EPA agrees with FDA that the terms "computer" or "computer driven" do not adequately reflect the data collection and storage technologies currently used by testing facilities. The Agency believes that the proposed term "automated data collection" provides a more appropriate description of the data collection and storage systems available for industry use.

17. *Section 160.135 Physical and chemical characterization studies.* EPA proposes to add § 160.135 in order to specify the provisions of the proposed FIFRA GLP standards which will not apply to studies designed to determine the physical and chemical characteristics of a test, control, or reference substance. Most studies designed to determine the physical or chemical characteristics of a test, control, or reference substance rarely involve any modifications to the protocol or experimental design and are usually conducted in an assembly line fashion. Therefore, proposed § 160.135(a) relaxes the requirements of the GLP standards without compromising the quality or integrity of data generated from these studies.

However, in § 160.135(b), EPA is also proposing that the exemptions listed in proposed § 160.135(a) will not apply to studies designed to determine stability, solubility, octanol water partition coefficient, volatility, and persistence of a test, control, or reference substance. These types of physical and chemical characterization studies are more complex in design, execution, and interpretation, and EPA does not believe that it can be assured of the quality and integrity of data generated from these studies without complete GLP compliance.

18. *Section 160.185 Reporting of study results.* a. In § 160.185(a)(5), EPA is proposing to require that the final report include information relating to the solubility, in addition to stability, of the test, control or reference substance if solubility information was important to the conduct of the experiment. This change is consistent with the proposed modification to §§ 160.105(b) and 160.113(a)(2) (see discussion of proposed §§ 160.105(b) and 160.113(a)(2)).

19. *Section 160.190 Storage and retrieval of records and data.* a. In § 160.190(a), EPA proposes to conform to the revised FDA GLP regulations by modifying this section to state that specimens obtained from mutagenicity tests and specimens of blood, urine, feces, and biological fluids generated as a result of a study need not be retained. EPA is also proposing that § 160.190(a) state that specimens of soil, water, and plants obtained from environmental testing need not be retained. EPA agrees with FDA's conclusion that retention of these specimens beyond initial evaluation is burdensome and does not have a significant impact on the quality of a study.

b. As in the revised FDA GLPs, EPA proposes to revise § 160.190(e) by deleting the requirement that study materials which are retained in archives must be indexed specifically by test substance, date of study, test system, and nature of study. EPA agrees with FDA that the intent of this section is to require indexing of materials in such a way as to permit expedient retrieval from archives. EPA does not believe it is necessary to stipulate the specific indexing terms which must be used.

20. *Section 160.195 Retention of records.* a. In § 160.195, EPA proposes to delete the examples provided in the first sentence of paragraph (c). EPA has proposed this change in conformity with FDA's recent revision because EPA agrees with FDA that these examples do not clarify which materials must be retained from a study, and therefore, are not necessary in this section.

b. EPA is also proposing to modify § 160.195(c) to state that specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, biological fluids, do not need to be retained beyond quality assurance review. This change has been adopted in order to be consistent with the change discussed in proposed § 160.190(a).

c. In new § 160.195(i), EPA proposes to allow records and other "raw data" required by these regulations to be retained either as original records or as true copies, such as photocopies, microfiche, or other accurate reproductions of the original records. This provision would be incorporated in the FIFRA GLPs, in § 160.195(i), in order

to be consistent with the recent changes to FDA's Good Laboratory Practice Regulations.

II. Economic Analysis

In order to satisfy requirements for analysis as specified by Executive Order 12291 and the Regulatory Flexibility Act, the Agency developed a document entitled "Regulatory Impact Analysis of the FIFRA Good Laboratory Practices Regulations". This document, which is available for public inspection, estimates the costs of compliance with the proposed revisions to the FIFRA Good Laboratory Practices Regulations. Compliance costs were estimated using data from a survey of laboratories potentially affected by the revised GLP regulation and from data on pesticides testing demand and costs taken from a 1980 study of the pesticides testing industry.

It was found that the GLP revisions will not increase the costs of health effects testing and that non-health effects testing costs will increase by about 20 percent. It is estimated that the adoption of the proposed GLP revisions would increase annual pesticide testing costs by between $6.3 and $9.9 million in 1986 dollars.

III. Statutory Requirements

As required by FIFRA section 25, copies of this proposed rule were provided to the Scientific Advisory Panel, the Secretary of Agriculture, the Senate Committee on Agriculture, Nutrition, and Forestry, and the House Committee on Agriculture. No comments were received from either Congressional Committee and the FIFRA Scientific Advisory Panel waived its review of this proposal. The following are the comments of the Secretary of the Department of Agriculture and the response of EPA:

The Secretary of the Department of Agriculture requested that the definition of "study" be modified to more clearly reflect EPA's intent that GLP compliance for efficacy testing be limited to product performance as required by 40 CFR 158.160. We have modified the definition of "study" accordingly.

The Secretary asked if the regulation requires that only studies conducted in accordance with the GLPs are acceptable for Agency review and, are there any conditions under which a study can be accepted which did not fully comply with the GLPs?

Studies may be submitted to EPA which do not completely conform to the GLPs as long as the Statement of Compliance, required by § 160.12(b) of the GLP regulations, describes in detail all differences between the practices used in the study and those required by the GLPs. EPA will review these studies. However, EPA will decide on a case-by-case basis whether studies which deviate from the GLPs are acceptable to support the pesticide product registration, or other marketing and research permit.

The Secretary of Agriculture asked if studies which reflect negatively on a chemical use, or studies which report toxic or carcinogenic effects will automatically be ignored by EPA if they have not been conducted under verifiable GLP conditions.

EPA will *not* ignore scientific data which does not comply with the FIFRA GLP standards, and may choose to rely on such data for purposes of showing adverse effects. However, as stated by § 160.17(a) of the FIFRA GLPs, EPA may determine that data which does not comply with the GLPs is not reliable to support an application for a research or marketing permit. Further, § 160.15(b) of the GLPs states that "The determination that a study will not be considered in support of an application for a research or marketing permit does not, however, relieve the applicant for such a permit of any obligation under any applicable statute or regulation to submit the results of the study to EPA." Adverse effects data, which is required to be submitted to the Agency under FIFRA section 6(a)(2), must be submitted to the Agency regardless of whether it complies with the GLPs or not. The Agency does not now, and will not in the future, require FIFRA section 6(a)(2) data to be generated and submitted to the Agency in accordance with the GLPs. EPA will not ignore any FIFRA section 6(a)(2) data. However, additional testing required by the Agency as a result of the FIFRA section 6(a)(2) finding must be conducted in accordance with the GLPs.

The Department of Agriculture commented that if they are required to conduct the analyses described in §§ 160.105 and 160.113, it would greatly limit their resources and capability to conduct studies under the minor use pesticide program. They state that they are working with labeled pesticides which already have tolerances established in food crops, and that are being utilized under simulated commercial conditions. Therefore, they believe that the information gained from these analyses would not be of any real significance to the results of the studies for efficacy, phytotoxicity, and residue.

EPA continues to believe that adequate test, control, and reference substance characterization, and knowledge of their behavior in the mixture is essential to assure the quality and integrity of the test. EPA agrees that the analyses of a test, control, or reference substance mixed with a carrier, as required by § 160.113, may be costly. However, some cost savings can be realized by obtaining the documentation of the identity, strength, purity, and composition for each batch of the test, control, and reference substance, as required by § 160.105, from the manufacturer of these chemicals (this is particularly pertinent when the chemical is specifically synthesized for the test). These analyses do not have to be repeated by the testing facility.

Finally, please note, the analyses required by §§ 160.105 and 160.113 are only required for efficacy testing of the types of products specified by 40 CFR 158.160 (e.g., for pesticide products that claim to control microorganisms that pose a threat to human health and pesticides that claim to control vertebrates that may transmit diseases to humans). Therefore, in most cases efficacy testing that is conducted under the Department of Agriculture's minor use pesticide program is not required to comply with the requirements of the GLPs, including the analyses required by §§ 160.105 and 160.113.

Finally, the Secretary of the Department of Agriculture asked if there is a grandfather provision for studies conducted prior to the implementation of the regulations.

EPA does not intend to require compliance with the revised GLP standards for studies begun significantly before the effective date of the final version of these proposed regulations.

IV. Other Regulatory Requirements

A. Executive Order 12291

Under Executive Order 12291, EPA is required to judge whether a rule is a "major" one and is therefore subject to the requirement of a Regulatory Impact Analysis. The proposed amendments of the FIFRA Good Laboratory Practice Standards would not be a major rule because they do not meet any of the criteria set forth and defined in section 1(b) of the Order.

B. Regulatory Flexibility Act

This rule has been reviewed under the Regulatory Flexibility Act of 1980 (Pub. L. 96-354; 94 Stat. 1165 (5 U.S.C. 60 et. seq.)) and it has been determined that it will not have significant economic impact on a substantial number of small businesses, small governments, or small organizations.

C. Paperwork Reduction Act

The Office of Management and Budget (OMB) has approved the information collection requirements contained in this proposed rule under the provisions of the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*, and has assigned OMB control numbers: 2070-0024, 2070-0032, 2070-0040, 2070-0055, 2070-0057, 2070-0060. Comments on these requirements should be submitted to the Office of Information and Regulatory Affairs of OMB, marked "Attention: Desk Officer for EPA." The final rule will respond to any OMB or public comments on the information collection requirements.

List of Subjects in 40 CFR Part 160

Good laboratory practices, Laboratories, Environmental protection, Hazardous materials, Chemicals, Recordkeeping and reporting requirements.

Dated: December 8, 1987.

Lee M. Thomas,

Administrator.

Therefore, it is proposed that 40 CFR Part 160 be amended as follows:

PART 160—[AMENDED]

1. The authority citation for Part 160 continues to read as follows:

Authority: 7 U.S.C. 136a, 136c, 136d, 136f, 136j, 136l, 136v, 136w; 21 U.S.C. 346a, 348, 371, Reorganization Plan No. 3 of 1970.

2. In § 160.3, by removing the alphabetical paragraph designations in paragraphs (a) through (q); by revising the definitions for "Control substance," "Study," and "Test system"; by replacing the term "Test substance or mixture" with the term "Test substance"; and by alphabetically inserting definitions for "Carrier", "Experimental start date", "Experimental termination date", "Reference Substance", "Study completion date", "Study initiation date", and "Vehicle", to read as follows:

§ 160.3 Definitions.

* * * * *

"Carrier" means any material (e.g., feed, water, soil, nutrient media) with which the test substance is combined for administration to test organisms.

"Control substance" means any chemical substance or mixture or any other material other than a test substance, feed, or water that is administered to the test system in the course of study for the purpose of establishing a basis for comparison with the test substance for no-effect levels.

* * * * *

"Experimental start date" means the first date the test substance is applied to the test system.

"Experimental termination date" means the last date on which data are collected directly from the study.

* * * * *

"Reference substance" means any chemical substance or mixture or material other than a test substance, feed, or water that is administered to or used in analyzing the test system in the course of a study for purposes of establishing a basis for comparison with the test substance for known effect levels.

* * * * *

"Study" means any experiment in which a test substance is studied in a test system under laboratory conditions or in the environment to determine or help predict its effects, metabolism, product performance (efficacy as required by 40 CFR 153.160), environmental and chemical fate, persistence and residue, or other characteristics in humans, other living organisms, or media. The term does not include basic exploratory studies carried out to determine whether a test substance has any potential utility.

"Study completion date" means the date the final report is signed by the study director.

* * * * *

"Study initiation date" means the date the protocol is signed by the study director.

"Test substance" means a substance or mixture administered or added to a test system in a study, which substance or mixture:

(1) Is the subject of an application for a research or marketing permit supported by the study, or is the contemplated subject of such an application; or

(2) Is an ingredient, impurity, degradation product, metabolite, or radioactive isotope of a substance described by paragraph (1) of this definition, or some other substance related to a substance described by that paragraph, which is used in the study to assist in characterizing the toxicity, metabolism, or other characteristics of a substance described by that paragraph.

"Test system" means any animal, plant, microorganism, chemical or physical matrix (e.g., soil or water), or subparts thereof, to which the test or control substance is administered or added for study. "Test system" also includes appropriate groups or components of the system not treated with the test, control, or reference substance.

* * * * *

"Vehicle" means any agent which facilitates the mixture, dispersion, or solubilization of a test substance with a carrier.

3. In § 160.29, by revising paragraphs (d), (e), and (f) to read as follows:

§ 160.29 Personnel.

* * * * *

(d) Personnel shall take necessary personal sanitation and health precautions designed to avoid contamination of test, control, and reference substances and test systems.

(e) Personnel engaged in a study shall wear clothing appropriate for the duties they perform. Such clothing shall be changed as often as necessary to prevent microbiological, radiological, or chemical contamination of test systems and test, control, and reference substances.

(f) Any individual found at any time to have an illness that may adversely affect the quality and integrity of the study shall be excluded from direct contact with test systems, and test, control, and reference substances, and any other operation or function that may adversely affect the study until the condition is corrected. All personnel shall be instructed to report to their immediate supervisors any health or medical conditions that may reasonably be considered to have an adverse effect on a study.

4. In § 160.31, by revising paragraph (b) to read as follows:

§ 160.31 Testing facility management.

* * * * *

(b) Replace the study director promptly if it becomes necessary to do so during the conduct of a study.

* * * * *

5. In § 160.35, by revising paragraphs (a) and (b) (1) and (3) and removing paragraph (e) to read as follows:

§ 160.35 Quality assurance unit.

(a) A testing facility shall have a quality assurance unit which shall be responsible for monitoring each study to assure management that the facilities, equipment, personnel, methods, practices, records, and controls are in conformance with the regulations in this part. For any given study, the quality assurance unit shall be entirely separate from and independent of the personnel engaged in the direction and conduct of that study.

(b) The quality assurance unit shall:

(1) Maintain a copy of a master schedule sheet of all studies conducted at the testing facility indexed by test substance and containing the test system, nature of study, date study was

initiated, current status of each study, identity of the sponsor, and name of the study director.

• • • • •

(3) Inspect each study at intervals adequate to ensure the integrity of the study and maintain written and properly signed records of each periodic inspection showing the date of the inspection, the study inspected, the phase or segment of the study inspected, the person performing the inspection, findings and problems, action recommended and taken to resolve existing problems, and any scheduled date for reinspection. Any problems which are likely to affect study integrity found during the course of an inspection shall be brought to the attention of the study director and management immediately.

• • • • •

6. By revising § 160.41 to read as follows:

§ [illegible] General.

[illegible]ting facility shall be of s[illegible]ze and construction to f[illegible]he proper conduct of studies. T[illegible]ilities which are not located within [illegible]ndoor controlled environment shall be of suitable location to facilitate the proper conduct of studies. Testing facilities shall be designed so that there is a degree of separation that will prevent any function or activity from having an adverse effect on the study.

7. By revising § 160.43 to read as follows:

§ 160.43 Test system care facilities.

(a) A testing facility shall have a sufficient number of animal rooms or other test system areas, as needed, to ensure: proper separation of species or test systems, isolation of individual projects, quarantine or isolation of animals or other test systems, and routine or specialized housing of animals or other test systems.

(1) In tests with plants or aquatic animals, proper separation of species can be accomplished within a room or area by housing them separately in different chambers or aquaria. Separation of species is unnecessary where the protocol specifies the simultaneous exposure of two or more species in the same chamber, aquarium, or housing unit.

(2) Aquatic toxicity tests for individual projects shall be isolated to the extent necessary to prevent cross-contamination of different chemicals used in different tests.

(b) A testing facility shall have a number of animal rooms or other test system areas separate from those described in paragraph (a) of this section to ensure isolation of studies being done with test systems or test, control, and reference substances known to be biohazardous, including volatile substances, aerosols, radioactive materials, and infectious agents.

(c) Separate areas shall be provided, as appropriate, for the diagnosis, treatment, and control of laboratory test system diseases. These areas shall provide effective isolation for the housing of test systems either known or suspected of being diseased, or of being carriers of disease, from other test systems.

(d) Facilities shall have proper provisions for collection and disposal of contaminated water, soil, or other spent materials. When animals are housed, facilities shall exist for the collection and disposal of all animal waste and refuse or for safe sanitary storage of waste before removal from the testing facility. Disposal facilities shall be so provided and operated as to minimize vermin infestation, odors, disease hazards, and environmental contamination.

(e) Facilities shall have provisions to regulate environmental conditions (e.g., temperature, humidity, photoperiod) as specified in the protocol.

(f) For marine test organisms, an adequate supply of clean sea water or artificial sea water (prepared from deionized or distilled water and sea salt mixture) shall be available. The ranges of composition shall be as specified in the protocol.

(g) For freshwater organisms, an adequate supply of clean water of the appropriate hardness, pH, and temperature, and free of contaminants capable of interfering with the study, shall be available as specified in the protocol.

(h) For plants, an adequate supply of soil of the appropriate composition, as specified in the protocol, shall be available as needed.

8. By revising § 160.45 to read as follows:

§ 160.45 Test system supply facilities.

(a) There shall be storage areas, as needed, for feed, nutrients, soils, bedding, supplies, and equipment. Storage areas for feed nutrients, soils, and bedding shall be separated from areas housing the test systems and shall be protected against infestation or contamination. Perishable supplies shall be preserved by appropriate means.

(b) When appropriate, plant supply facilities shall be provided. These include:

(1) Facilities, as specified in the protocol, for holding, culturing, and maintaining algae and aquatic plants.

(2) Facilities, as specified in the protocol, for plant growth (e.g., greenhouses, growth chambers, light banks).

(c) When appropriate, facilities for aquatic animal tests shall be provided. These include aquaria, holding tanks, ponds, and ancillary equipment, as specified in the protocol.

9. By revising § 160.47 to read as follows:

§ 160.47 Facilities for handling test, control, and reference substances.

(a) As necessary to prevent contamination or mixups, there shall be separate areas for:

(1) Receipt and storage of the test, control, and reference substances.

(2) Mixing of the test, control, and reference substances with a carrier, e.g., feed.

(3) Storage of the test, control, and reference substance mixtures.

(b) Storage areas for test, control, and/or reference substance and for test, control, and/or reference mixtures shall be separate from areas housing the test systems and shall be adequate to preserve the identity, strength, purity, and stability of the substances and mixtures.

10. By revising § 160.49 to read as follows:

§ 160.49 Laboratory operation areas.

Separate laboratory space and other space shall be provided, as needed, for the performance of the routine and specialized procedures required by studies.

§ 160.53 [Removed]

11. By removing § 160.53 *Administrative and personnel facilities.*

12. By revising § 160.61 to read as follows:

§ 160.61 Equipment design.

Equipment used in the generation, measurement, or assessment of data and equipment used for facility environmental control shall be of appropriate design and adequate capacity to function according to protocol and shall be suitably located for operation, inspection, cleaning, and maintenance.

13. In § 160.63, by revising paragraph (b) to read as follows:

§ 160.63 Maintenance and calibration of equipment.

• • • • •

(b) The written standard operating procedures required under

§ 160.81(b)(11) shall set forth in sufficient detail the methods, materials, and schedules to be used in the routine inspection, cleaning, maintenance, testing, calibration, and/or standardization of equipment, and shall specify, when appropriate, remedial action to be taken in the event of failure or malfunction of equipment. The written standard operating procedures shall designate the person responsible for the performance of each operation.

* * * * *

14. In § 160.81, by revising paragraphs (b) (1), (2), (3), (5), (6), (7), and (12) and (c) to read as follows:

§ 160.81 Standard operating procedures.

* * * * *

(b) * * *

(1) Test system room preparation.

(2) Test system care.

(3) Receipt, identification, storage, handling, mixing, and method of sampling of the test, control, and reference substances.

* * * * *

(5) Laboratory or other tests.

(6) Handling of test systems found moribund or dead during study.

(7) Necropsy of test systems or postmortem examination of test systems.

* * * * *

(12) Transfer, proper placement, and identification of test systems.

(c) Each laboratory or other study area shall have immediately available manuals and standard operating procedures relative to the laboratory or field procedures being performed. Published literature may be used as a supplement to standard operating procedures.

* * * * *

15. By revising § 160.90 to read as follows:

§ 160.90 Animal and other test system care.

(a) There shall be standard operating procedures for the housing, feeding, handling, and care of animals and other test systems.

(b) All newly received test systems from outside sources shall be isolated and their health status or appropriateness for the study evaluated. This evaluation shall be in accordance with acceptable veterinary medical practice or scientific practice.

(c) At the initiation of a study, test systems shall be free of any disease or condition that might interfere with the purpose or conduct of the study. If during the course of the study, the test systems contract such a disease or condition, the diseased test systems should be isolated, if necessary. These test systems may be treated for disease or signs of disease provided that such treatment does not interfere with the study. The diagnosis, authorization of treatment, description of treatment, and each date of treatment shall be documented and shall be retained.

(d) Warm-blooded animals, adult reptiles, and adult terrestrial amphibians used in laboratory procedures that require manipulations and observations over an extended period of time or in studies that require these test systems to be removed from and returned to their test system-housing units for any reason (e.g., cage cleaning, treatment, etc.), shall receive appropriate identification (e.g., tattoo, toe clip, color code, ear tag, ear punch, etc.). All information needed to specifically identify each test system within the test system-housing unit shall appear on the outside of that unit. Suckling mammals and juvenile birds are excluded from the requirement of individual identification unless otherwise specified in the protocol.

(e) Except as specified in paragraph (e)(1) of this section, test systems of different species shall be housed in separate rooms when necessary. Test systems of the same species, but used in different studies, should not ordinarily be housed in the same room when inadvertent exposure to test, control, or reference substances or test system mixup could affect the outcome of either study. If such mixed housing is necessary, adequate differentiation by space and identification shall be made.

(1) Plants, invertebrate animals, aquatic vertebrate animals, and organisms that may be used in multispecies tests need not be housed in separate rooms, provided that they are adequately segregated to avoid mixup and cross contamination.

(2) [Reserved]

(f) Cages, racks, pens, enclosures, aquaria, holding tanks, ponds, growth chambers, and other holding, rearing and breeding areas, and accessory equipment, shall be cleaned and sanitized at appropriate intervals.

(g) Feed, soil, and water used for the test systems shall be analyzed periodically to ensure that contaminants known to be capable of interfering with the study and reasonably expected to be present in such feed, soil, or water are not present at levels above those specified in the protocol. Documentation of such analyses shall be maintained as raw data.

(h) Bedding used in animal cages or pens shall not interfere with the purpose or conduct of the study and shall be changed as often as necessary to keep the animals dry and clean.

(i) If any pest control materials are used, the use shall be documented. Cleaning and pest control materials that interfere with the study shall not be used.

(j) All plant and animal test organisms shall be acclimatized, prior to their use in an experiment, to the environmental conditions of the test.

Subpart F—Test, Control, and Reference Substances

16. By revising the heading for Subpart F to read as set forth above.

17. By revising § 160.105 to read as follows:

§ 160.105 Test, control, and reference substance characterization.

(a) The identity, strength, purity, and composition, or other characteristics which will appropriately define the test, control, or reference substance shall be determined for each batch and shall be documented before its use in an experiment. Methods of synthesis, fabrication, or derivation of the test, control, or reference substance shall be documented by the sponsor or the testing facility.

(b) The stability and, when relevant to the conduct of the experiment, the solubility of each test, control, or reference substance shall be determined by the testing facility or by the sponsor before the experimental start date. Where periodic analysis of each batch is required by the protocol, there shall be written standard operating procedures that shall be followed.

(c) Each storage container for a test, control, or reference substance shall be labeled by name, chemical abstracts service number (CAS) or code number, batch number, expiration date, if any, and, where appropriate, storage conditions necessary to maintain the identity, strength, purity, and composition of the test, control, or reference substance. Storage containers shall be assigned to a particular test substance for the duration of the study.

(d) For studies of more than 4 weeks duration, reserve samples from each batch of test, control, and reference substances shall be retained for the period of time provided by § 160.195.

(e) The stability of test, control, and reference substances under test conditions shall be known for all studies.

18. In § 160.107, by revising the section heading and introductory text to read as follows:

§ 160.107 Test, control, and reference substance handling.

Procedures shall be established for a system for the handling of the test, control, and reference substances to ensure that:

• • • • •

19. By revising § 160.113 to read as follows:

§ 160.113 Mixtures of substances with carriers.

(a) For each test, control, or reference substance that is mixed with a carrier, tests by appropriate analytical methods shall be conducted:

(1) To determine the uniformity of the mixture and to determine, periodically, the concentration of the test, control, or reference substance in the mixture.

(2) To determine the stability and, when relevant to the conduct of the experiment, the solubility of the test, control, or reference substance in the mixture before the experimental start [illegible] termination of the stability and [illegible] of the test, control, or [illegible] bstance in the mixture shall [illegible] under the environmental [illegible] is specified in the protocol and as required by the conditions of the experiment. Where periodic analysis of the mixture is required by the protocol, there shall be written standard operating procedures that shall be followed.

(b) Where any of the components of the test, control, or reference substance [illegible] ire has an expiration date, that [illegible] shall be clearly shown on the [illegible] r. If more than one component has an expiration date, the earliest date shall be shown.

(c) If a vehicle is used to facilitate the mixing of a test substance with a carrier, assurance shall be provided that the vehicle does not interfere with the integrity of the test.

20. In § 160.120, by revising paragraph (a) to read as follows:

§ 160.120 Protocol.

(a) Each study shall have an approved written protocol that clearly indicates the objectives and all methods for the conduct of the study. The protocol shall contain but shall not necessarily be limited to the following information:

(1) A descriptive title and statement of the purpose of the study.

(2) Identification of the test, control, and reference substance by name, chemical abstracts service (CAS) number or code number.

(3) The name and address of the sponsor and the name and address of the testing facility at which the study is being conducted.

(4) The proposed experimental start and termination dates.

(5) Justification for selection of the test system.

(6) Where applicable, the number, body weight, sex, source of supply, species, strain, substrain, and age of the test system.

(7) The procedure for identification of the test system.

(8) A description of the experimental design, including methods for the control of bias.

(9) Where applicable, a description and/or identification of the diet used in the study as well as solvents, emulsifiers and/or other materials used to solubilize or suspend the test, control, or reference substances before mixing with the carrier. The description shall include specifications for acceptable levels of contaminants that are reasonably expected to be present in the dietary materials and are known to be capable of interfering with the purpose or conduct of the study if present at levels greater than established by the specifications.

(10) The route of administration and the reason for its choice.

(11) Each dosage level, expressed in milligrams per kilogram of body or test system weight or other appropriate units, of the test, control, or reference substance to be administered and the method of frequency of administration.

(12) The type and frequency of test analyses, and measurements to be made.

(13) The records to be maintained.

(14) The date of approval of the protocol by the sponsor and the dated signature of the study director.

(15) A statement of the proposed statistical method.

• • • • •

21. In § 160.130, by revising paragraphs (d) and (e) to read as follows:

§ 160.130 Conduct of a study.

• • • • •

(d) In animal studies where histopathology is required, records of gross findings for a specimen from postmortem observations shall be available to a pathologist when examining that specimen histopathologically.

(e) All data generated during the conduct of a study, except those that are generated by automated data collection systems, shall be recorded directly, promptly, and legibly in ink. All data entries shall be dated on the day of entry and signed or initialed by the person entering the data. Any change in entries shall be made so as not to obscure the original entry, shall indicate the reason for such change, and shall be dated and signed or identified at the time of the change. In automated data collection systems, the individual responsible for direct data input shall be identified at the time of data input. Any change in automated data entries shall be made so as not to obscure the original entry, shall indicate the reason for change, shall be dated, and the responsible individual shall be identified.

22. By adding § 160.135 to read as follows:

§ 160.135 Physical and chemical characterization studies.

(a) Except as provided in paragraph (b) of this section, the following provisions shall not apply to studies designed to determine physical and chemical characteristics of a test, control, or reference substance:

§ 160.31 (c), (d), and (g)
§ 160.35 (b) and (c)
§ 160.43
§ 160.45
§ 160.47
§ 160.49
§ 160.61(b) (1), (2), (6) through (9), and (12)
§ 160.90
§ 160.105 (a) through (d)
§ 160.113
§ 160.120(a) (5) through (12), and (15)
§ 160.185(a) (5) through (8), (10), (12), and (14)
§ 160.195 (c) and (d)

(b) The exemptions provided in paragraph (a) of this section shall not apply to physical/chemical characterization studies designed to determine stability, solubility, octanol water partition coefficient, volatility, and persistence (such as biodegradation, photodegradation, and chemical degradation studies), and such studies shall be conducted in accordance with this part.

23. In § 160.185, by revising paragraphs (a) (4) and (5) to read as follows:

§ 160.185 Reporting of study results.

(a) • • •

(4) The test, control, and reference substances identified by name, chemical abstracts service (CAS) number or code number, strength, purity, and composition, or other appropriate characteristics.

(5) Stability and, when relevant to the conduct of the experiment, the solubility of the test, control, and reference substances under the conditions of administration.

• • • • •

24. In § 160.190, by revising paragraphs (a) and (e) to read as follows:

§ 160.190 Storage and retrieval of records and data.

(a) All raw data, documentation, records, protocols, specimens, and final reports generated as a result of a study shall be retained. Specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, and biological fluids, do not need to be retained beyond quality assurance. Correspondence and other documents relating to interpretation and evaluation of data, other than those documents contained in the final report, also shall be retained.

• • • • •

(e) Material retained or referred to in the archives shall be indexed to permit expedient retrieval.

25. In § 160.195, by revising paragraph (c) and adding paragraph (i) to read as follows:

§ 160.195 Retention of records.

• • • • •

(c) Wet specimens, samples of test, control, or reference substances, and specially prepared material which are relatively fragile and differ markedly in stability and quality during storage, shall be retained only as long the quality of the preparation affords evaluation. Specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, biological fluids, do not need to be retained beyond quality assurance review. In no case shall retention be required for longer periods than those set forth in paragraph (b) of this section.

• • • • •

(i) Records required by this part may be retained either as original records or as true copies such as photocopies, microfilm, microfiche, or other accurate reproductions of the original records.

[FR Doc. 87-29511 Filed 12-24-87; 8:45 am]

BILLING CODE 6560-50-M

---

40 CFR Part 792

[OPTS-46016; FRL-3245-6]

Toxic Substances Control Act (TSCA); Good Laboratory Practice Standards

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: EPA is proposing to amend the TSCA Good Laboratory Practice (GLP) Standards to incorporate many of the changes made by the Food and Drug Administration (FDA) to its GLP regulations and to expand the scope of the TSCA GLP standards to apply to testing conducted in the field under TSCA. EPA is proposing this amendment in order to ensure the quality and integrity of data generated from such studies.

DATE: Submit written comments on or before March 28, 1988.

ADDRESS: Submit written comments, identified by the document control number (OPTS-46016), in triplicate to: TSCA Public Information Office (TS-793), Office of Pesticides and Toxic Substances, Environmental Protection Agency, Rm. NE-G004, 401 M St., SW., Washington, DC 20460.

The public record supporting this action is available for inspection at the above address from 8 a.m. to 4 p.m., Monday through Friday, except legal holidays.

FOR FURTHER INFORMATION CONTACT: Edward A. Klein, Director, TSCA Assistance Office (TS-799), Office of Toxic Substances, Rm. E-543, 401 M St., SW., Washington, DC 20460 (202) 554-1404.

SUPPLEMENTARY INFORMATION: Following is an index to the remainder of this preamble:

I. Introduction

A. Legal Authority

On November 29, 1983 (48 FR 53922), EPA promulgated the GLP standards under the authority of TSCA section 4 (90 Stat. 2006, 15 U.S.C. 2603). Section 4(a) of TSCA authorizes the EPA Administrator to require, by rule, that manufacturers (including importers) and processors of identified chemical substances and mixtures test such chemicals if certain findings are made. Section 4(b)(1) of TSCA specifies that each test rule shall include standards for the development of test data. These standards are defined in section 3(12) of TSCA to mean a prescription of—

(A) the—

(i) health and environmental effects, and

(ii) information relating to the toxicity, persistence, and other characteristics which affect health and the environment, for which test data for a chemical substance or mixture are to be developed and any analysis that is to be performed on such data, and

(B) to the extent necessary to assure that data respecting such effects and characteristics are reliable and adequate—

(i) the manner in which such data are to be developed,

(ii) the specification of any test protocol or methodology to be employed in the development of such data, and

(iii) such other requirements as are necessary to provide such assurance.

In summary, the specific authority to issue the GLP standards is provided by section 4(b)(1) of TSCA, which is further explained by the definitions in sections 3(12)(B)(i) and 3(12)(B)(iii).

In addition, the Agency also requires sponsors to utilize these GLP standards when conducting testing under TSCA section 4 testing consent agreements and will include provisions to adhere to these GLP standards in those agreements (see 40 CFR 790.60(a)(7)). Also, it is the Agency's policy that all data developed as a result of rules or orders under section 5 of TSCA should be in accordance with the GLP standards. If data developed under section 5 of TSCA are not generated in accordance with the GLP standards, the Agency may elect to consider such data insufficient to evaluate the health effects, environmental effects, and fate of the chemical.

B. Background

EPA originally published enforceable TSCA Good Laboratory Practice Standards in the Federal Register of November 29, 1983 (48 FR 53922), which were codified as 40 CFR Part 792. At the same time, EPA published GLP standards applicable to testing under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, 48 FR 53963, 40 CFR Part 160). These regulations were promulgated in response to investigations by EPA and FDA during the mid-1970s which revealed that some studies submitted to the Agencies had not been conducted in accordance with acceptable laboratory practices. Some studies had been conducted so poorly that the resulting data could not be relied upon in EPA's regulatory decisionmaking process. For instance, some studies had been submitted which did not adhere to specified protocols, were conducted by underqualified personnel and supervisors, or were not adequately monitored by study sponsors. In some cases results were selectively reported, underreported, or fraudulently reported. In addition, it was discovered that some testing facilities displayed poor animal care procedures and inadequate recordkeeping techniques. The TSCA GLP standards specify minimum practices and

procedures which must be followed in order to ensure the quality and integrity of data submitted in accordance with TSCA section 4 requirements. The 1983 TSCA GLP standards also established a policy that persons should comply with GLP standards when submitting data in response to rules and orders issued under section 5 of TSCA, and when submitting data to the Agency voluntarily.

When EPA published its final TSCA and FIFRA GLP standards in the Federal Register of November 29, 1983, the Agency sought to harmonize the requirements and language with those regulations promulgated by the FDA in the Federal Register of December 22, 1978 (43 FR 60013), and codified as 21 CFR Part 58. Differences between the two Agencies' current GLP regulations exist only to the extent necessary to reflect the Agencies different statutory responsibilities under TSCA, FIFRA, and the Federal Food, Drug, and Cosmetic Act (FFDCA). Similar to the FDA GLP regulations, the FIFRA and TSCA GLPs delineate standards for studies designed to determine the health effects of a test substance; however, the TSCA GLPs also contain provisions related to environmental testing (i.e., ecological effects and chemical fate).

Compliance with EPA's GLP regulations has been monitored through a program of laboratory inspections and study audits coordinated between EPA and FDA. Under an Interagency Agreement originating in 1978, FDA carries out inspections at laboratories which conduct health effects testing. EPA primarily performs laboratory inspections and data audits for environmental studies.

After a thorough review of its GLP regulations and compliance program, FDA concluded that some of the provisions of the GLPs needed to be clarified, amended, or deleted in order to reduce the regulatory burden on testing facilities. Accordingly, FDA proposed revisions to its GLP regulations in the Federal Register of October 24, 1984 (49 FR 43530), which were intended to simplify the regulation without compromising study integrity. FDA's proposed revision has recently been published as a final rule in the Federal Register of September 4, 1987 (52 FR 33768).

EPA agrees with FDA that many provisions of the GLP regulations can be streamlined without compromising the goals of the GLPs. Therefore, EPA is proposing to amend the TSCA GLP standards to incorporate many of the changes recently made by FDA to its GLP regulations. In addition, EPA is proposing to expand the scope of the TSCA GLPs to cover testing wherever it is conducted (e.g., field testing). In another notice in this Federal Register EPA is proposing similar changes to the FIFRA GLP standards.

C. Consistency With FDA GLP Regulations

It is EPA's policy to minimize the regulatory burden on the public which might arise from conflicting requirements which could be promulgated under different regulatory authorities. In keeping with this policy, the final 1983 TSCA GLP Standards, 40 CFR Part 792, followed the format and, with few exceptions, the wording of FDA's final GLP regulations, 21 CFR Part 58. Differences between the EPA and FDA GLP regulations were based upon varying needs and responsibilities under each Agency's regulatory statutes. This proposed revision to the TSCA GLP standards follows this same policy by conforming to many of the changes FDA made to its GLP regulations, published in the Federal Register of September 4, 1987 (52 FR 33768). EPA has varied from FDA's revised GLP regulations only when necessary due to EPA's statutory responsibilities. The most significant differences between the EPA proposal and the revised FDA GLP regulations are the scope of the testing and test systems affected.

As in the current TSCA Good Laboratory Practice Standards, the proposed revisions to the TSCA GLP standards vary from the FDA GLPs in that the TSCA GLPs incorporate GLP provisions for environmental testing (EPA is proposing that the FIFRA GLPs extend to environmental studies as well). Environmental studies include ecological effects and chemical fate studies. Ecological effects studies are those performed for development of information on nonhuman toxicity and potential ecological impact of chemicals and their degradation products. Chemical fate studies are studies performed to characterize physical, chemical, and persistence properties of a substance in order to evaluate the transport and transformation of the substance in the environment.

To ensure the quality and integrity of all data generated from environmental studies, the current TSCA GLP standards contain requirements within 40 CFR Part 792 Subpart L applicable to testing plants, microbial organisms, aquatic organisms, amphibians, reptiles, and birds, where appropriate. These requirements include provisions for core care facilities, and supply facilities for the various test systems used in environmental testing. As a means of simplifying the regulations, EPA is proposing that the requirements currently found within Subpart L be merged into Subparts A through J of the TSCA GLPs. Accordingly, it is proposed that current § 792.43 *Animal care facilities*, § 792.45 *Animal supply facilities*, and § 792.90 *Animal care* incorporate the provisions relating to the care of test systems, care facilities, and supply facilities from § 792.228 in Subpart L. The expanded sections are retitled in the proposed revision as follows: § 792.43 *Test system care facilities*, § 792.45 *Test system supply facilities*, and § 792.90 *Animal and other test system care*. Further, in most instances, EPA is proposing to replace the term "animal," currently used in the EPA and FDA GLP regulations, with the broader term "test system." Specifically, this change is proposed in §§ 792.43, 792.45, 792.81, 792.90, and 792.120. These proposed changes are further discussed in Unit I.D. of this preamble.

EPA's proposed TSCA GLP standards also vary from FDA's in their coverage of testing conducted in the field. To ensure the quality and integrity of data submitted to the Agency, EPA believes that GLP standards must apply whenever data collection occurs. Because many of the test data required by EPA are developed in the field, or more accurately in outdoor laboratories (i.e., ground water studies, air monitoring studies, degradation in soil, etc.), EPA is proposing to include field testing within the scope of these regulations.

The remaining differences between the EPA and FDA GLPs are described in the preamble to this proposed rule and the preamble to the TSCA Good Laboratory Practice Standards, published in the Federal Register of November 29, 1983 (48 FR 53922). EPA has coordinated this proposal with FDA and has considered comments received on the proposal to amend the FDA GLP regulations (October 29, 1984; 49 FR 43530).

D. Proposed Changes to the TSCA GLP Regulations

1. *Section 792.1 Scope.* EPA proposes to amend § 792.1 to reflect the Agency's option of entering into testing consent agreements in lieu of a test rule under section 4 of TSCA. Consistently, the term "testing consent agreement" has been added to the definition of "test substance" in proposed § 792.3, and has been added in proposed §§ 792.12 and 792.17.

2. *Section 792.3 Definitions.* a. EPA proposes that the definition of the term "carrier" be moved from § 792.226(b) to § 792.3. As stated in Unit I.C. of this

preamble. EPA is proposing to delete Subpart L and include all the provisions of Subpart L within Subparts A through J of the TSCA GLP standards. Therefore, EPA proposes to define the term "carrier" in § 792.3 to mean any material, such as feed, water, soil, nutrient material, etc., with which the test substance is combined for administration to test organisms.

b. EPA proposes to conform with the September 4, 1987, FDA GLP regulations by amending the definition of "control substance" to exclude feed and water. EPA agrees with FDA's statement regarding this change (52 FR 33769: September 4, 1987) that "the term control [substance] should be reserved for the discrete substances/articles, and vehicles other than feed and water administered to groups of the test system to provide a basis of comparison with the test [substance]."

FDA contends that, under the current definition of "control substance," because the control group of a test system provides the basis for comparison with a test substance, any substance administered to the control group is considered a control substance. This means that feed and water given to the control group of a study are considered a control substance. For instance, in studies in which the test substance or mixture is administered to the test system orally, through feed or drinking water, gavage, or injection, the feed or water is considered a control substance. As a control substance, the feed or water is subject to § 792.105(a) for substance characterization, § 792.105(b) for testing for stability and solubility, § 792.105(c) for requirements for appropriate storage, § 792.105(d) for retention of reserve samples, and § 792.107 for documentation of receipt and distribution of each batch. EPA agrees with FDA that placing these requirements on the use of feed and water as a control substance in control groups unnecessarily burdens the regulated community and is not essential for ensuring the quality and integrity of the data generated by a study.

However, under 40 CFR Part 792, feed and water used as a carrier for the test and control substances or mixtures are still covered by the applicable sections for the testing and storage of test, control, and reference substances and mixtures. For example, § 792.31(e) requires testing facility management to ensure that materials are available as scheduled; § 792.45 requires that test system supply facilities shall be provided to ensure proper feed storage; § 792.81(b)(2) requires Standard Operating Procedures (SOP) for test system care, including nutrition; § 792.90(g) requires periodic analysis of feed and water to ensure that contaminants which would interfere with the study are not present; § 792.120(a)(9) requires the protocol to describe and/or identify the diet used in the study, including the level of contaminants expected in the dietary materials.

c. EPA also proposes to modify the definition of "control substance" by adding the phrase "for no effect levels." This addition to the definition is being proposed merely to clarify the difference between the term "reference substance" and "control substance." While a control substance is used to determine a baseline comparison for no effect levels, a reference substance is used to determine a baseline comparison to an established effect level.

d. EPA proposes to add and define the terms "experimental start date" and "experimental termination date." "Experimental start date" is proposed to mean the first date the test substance is applied to the test system. Under this definition, as of the experimental start date: (1) Under proposed § 792.105(b), the stability and, if important to the conduct of the experiment, the solubility of the test, control, and reference substance would have to be determined; (2) under proposed § 792.113(a)(2), the stability and, when important to the conduct of the experiment, the solubility of the test, control, and reference substance in the mixture would have to be determined and; (3) under proposed § 792.120(a)(4), the proposed experimental start date would appear in the protocol.

EPA proposes that "experimental termination date" be defined as the last date on which data are collected directly from the study. Under § 792.120(a)(4), as proposed, EPA would require the proposed experimental termination date to appear in the protocol. EPA considers histopathology after scheduled terminal animal sacrifice to be carried out before the experimental termination date.

Experimental start and termination dates would be expressed as the actual calendar dates, not just time-line increments. Therefore, when determining the proposed experimental start and termination dates, as would be required by proposed § 792.120(a)(4), the submitter should consider any lag time relating to protocol approval and laboratory contracting.

e. EPA proposes to add and define the term "reference substance". This term is currently defined in § 792.226(f) to mean any chemical substance or mixture or material other than a test substance that is administered to or used in analyzing the test system in the course of a study for purposes of establishing a basis for comparison with the test substance. EPA proposes to add the phrase "for known effect levels" to this definition to more clearly distinguish the terms "reference substance" and "control substance" (see discussion of the term "control substance" in Unit I.D. of this preamble).

Consistent with the Agency's proposal to merge the provisions of Subpart L into Subparts A through J, all the requirements provided for test and control substances are being proposed to apply to "reference substances." Accordingly, the term "reference substance" has been added wherever the term "test and control substance" appears in these regulations. Specifically, it is proposed that the term "reference substance" be added to § 792.29 (d) through (f); § 792.43(b); § 792.47(a) (1) through (3) and (b); § 792.81(b)(3); § 792.90(e); the Subpart F heading; § 792.105 (a) through (e); § 792.107; § 792.113 (a) and (b); § 792.120(a) (2), (9), and (11); § 792.185(a) (4) and (5); and § 792.195(c).

f. EPA proposes to amend the definition of "sponsor" by replacing the term "negotiated testing agreement" with the term "testing consent agreement." This proposal reflects the Agency's option of entering into a section 4 testing consent agreement in lieu of a test rule promulgated under section 4 of TSCA.

g. EPA proposes to broaden the definition of the term "study" to be consistent with the scope of testing that may be submitted under TSCA sections 4 and 5.

EPA is proposing to delete the phrase "in vivo or in vitro" from the definition of "study." The Agency still intends the requirements of these regulations to apply to "in vivo and in vitro" experiments. However, since the Agency intends these regulations to apply to all studies required to be developed under TSCA, including those conducted in the field, EPA believes that the phrase "in vivo or in vitro" in the current definition of "study" is too limiting.

Further, EPA is proposing to delete the term "prospectively" from the definition of "study." In this way, epidemiological studies, which could be "retrospective," will be required to be presented to the Agency in accordance with the GLP standards. EPA recognizes that data used in an epidemiological study may not have been generated in conformance

with the TSCA GLP standards, however, it is EPA's contention that the epidemiological study itself can be conducted and submitted to the Agency in accordance with the GLPs.

EPA is also proposing to delete from the current definition of "study" the following sentence: "The term does not include studies utilizing human subjects or clinical studies or field trials in animals." Again, this change is consistent with EPA's intention that all studies follow GLPs which are required to be conducted under TSCA.

h. EPA proposes to incorporate the FDA definitions for "study completion date" and "study initiation date" into the TSCA GLP standards in § 792.3. "Study completion date" is proposed to mean the date the final report is signed by the study director. EPA advises that the phrase "close of the study" as used in § 792.33(f) refers to the "study completion date." Therefore, as of that date: (1) Under § 792.33(f), the study director must ensure that all raw data, documentation, protocols, specimens, and final reports are transferred to the archives; and (2) after this date under § 792.185(c), corrections or additions to the final report must be in the form of an amendment by the study director under the procedures specified in that section.

EPA proposes to define "study initiation date" as the date the protocol is signed by the study director. EPA advises that the phrase "study is initiated" as used in § 792.31(a), and the phrase "study was initiated" as used in § 792.35(b)(1) refer to the "study initiation date." Therefore, as of the study initiation date: (1) Under § 792.31(a), the testing facility management would designate a study director; (2) under § 792.35(b)(1), the study would be entered on the master schedule sheet by the quality assurance unit; and (3) under § 792.120(b), after this date all changes or revisions in the protocol would be documented, signed by the study director, and dated. EPA also expects that as of the study initiation date, under § 792.31(e), the testing facility management would have ensured that personnel resources, facilities, equipment, material, and methodologies are available as scheduled.

i. EPA proposes to replace the term "test substance or mixture" with the term "test substance." This is an editorial change which makes usage consistent in the GLP standards. The term "test substance" is proposed to be defined to include mixtures.

j. EPA proposes to incorporate the definition of the term "test system" currently found at § 792.228(a) into the definition of "test system" currently found at § 792.3(p). Therefore, the proposed definition of "test system" in proposed § 792.3 will include chemical or physical matrices (e.g., soil or water).

k. EPA proposes to incorporate the term "vehicle" currently found in § 792.228(g) into § 792.3 *Definitions.*

3. *Section 792.31 Testing facility management.* In conformance with the revised FDA GLP regulations, in § 792.31(b), EPA proposes to delete the requirement that the replacement of a study director must be documented as "raw data." EPA agrees with FDA that this requirement is redundant with other provisions of the GLPs. For instance, § 792.35(b)(1) states that the master schedule sheet must contain the name of the study director. As FDA notes (52 FR 33770), any replacement of the study director would be reflected on the master schedule sheet, which is already considered "raw data." Further, § 792.120(b) states that all changes in an approved protocol must be documented and signed by the study director. Replacement of the study director is considered to be a change in the approved protocol.

4. *Section 792.35 Quality assurance unit (QAU).* a. In § 792.35(a), EPA proposes to conform with the revised FDA GLP regulations by substituting the term "which" for the current phrase "composed of one or more individuals who." This change clarifies that EPA does not require the QAU to be a fixed, permanently staffed unit whose only functions are to monitor the quality of a study. The Agency is only concerned that there be a distinct separation of duties between those personnel involved with the conduct or direction of a study and those personnel performing quality assurance on the same study. Therefore, EPA does intend proposed § 792.35(a) to prohibit personnel from performing quality assurance activities on their own study.

b. In § 792.35(b)(1), EPA proposes to delete the requirement that the name of the study sponsor appear on the master schedule sheet. Instead, it is proposed that under § 792.35(b)(1) the sponsor's identity appear on the master schedule sheet. This change is being proposed to be consistent with the FDA's recent revision and to provide the regulated community the option of using an identity code on the master schedule in lieu of the sponsor's name.

EPA agrees with FDA's contention that requiring the sponsor to be identified specifically by name on the master schedule is not essential to fulfill the requirements of the GLPs or the goal of ensuring the quality and integrity of the data generated from the studies. However, while the name of the study sponsor would not be required to appear on the master schedule sheet, this information must be made available to the Agency upon request.

c. As in the revised FDA GLP regulations, EPA is also proposing to delete the requirement in § 792.35(b)(1) that the master schedule sheet contain the status of the final report. EPA agrees with FDA that this requirement is redundant in view of the other information required by § 792.35(b)(1) such as the date the experiment began and the current status of each study.

d. In conformance with the revised FDA GLP regulations, EPA proposes to modify the requirements of § 792.35(b)(3) to provide for inspections of a study on a schedule adequate to ensure the integrity of the study. This section currently specifies that the quality assurance unit must inspect each phase of a study periodically. This section also currently specifies that for studies lasting more than 6 months, quality assurance inspections shall be conducted every 3 months, and for studies lasting less than 6 months, quality assurance inspections shall be conducted at intervals adequate to ensure the integrity of the study.

The proposed changes to this section will allow the QAU the necessary latitude to adjust its monitoring activities to meet the individual problems of each study. EPA agrees with FDA's contention that an inspection of each phase of the study is not necessary to ensure that a study is being conducted properly. However, EPA also agrees with FDA that each study, no matter how short, must be inspected at least once while in process. EPA expects that by allowing the QAU flexibility in designing a reasonable inspection schedule, the goal of ensuring the quality of the study can be best achieved.

e. Consistent with the revised FDA GLPs, EPA is proposing to delete § 792.35(e) in its entirety. Section 792.35(e) currently requires that all quality assurance records be kept in one location at the testing facility. As FDA pointed out in its October 29, 1984, proposed GLP revision, since § 792.190(b) already requires the use of archives for the orderly storage and expedient retrieval of all reports and records, the requirements of § 792.35(e) are not necessary. However, EPA maintains that all reports and records, including those of the QAU, must be easily accessible and made available to EPA and FDA inspectors when requested.

5. *Section 792.41 General.* FDA has deleted from its GLPs the requirement

that the location of each testing facility be suitable to facilitate the proper conduct of studies. However, EPA is proposing that § 792.41 require that testing facilities which are not located within an indoor controlled environment be suitably located to facilitate the proper conduct of studies.

The studies FDA requires are generally conducted within the confines of a traditional indoor laboratory. Because the conditions specified within a protocol can be artificially manipulated within the traditional indoor laboratory, the location of these laboratories is generally not a factor in determining the quality of a study. Therefore, it is not necessary to ensure that a traditional indoor testing facility is suitably located to facilitate the proper conduct of the study.

However, the studies EPA requires are not necessarily conducted within the confines of the traditional indoor scientific laboratory (i.e., field studies, exposure monitoring studies, ecological toxicity studies, etc.). EPA considers any site where testing is undertaken to generate data required by the Agency to be a testing facility. The conditions required by the protocol are not necessarily conducive to artificial manipulation in the field, or other outdoor testing facilities. Therefore, ensuring the suitability of the location of these types of testing facilities is both a valid and necessary part of EPA's GLP Standards.

6. *Section 792.43 Test system care facilities.* a. EPA is proposing to revise the title of § 792.43 from "Animal care facilities" to "Test system care facilities." The proposed heading for § 792.43 more adequately reflects the Agency's intent to specify within the main body of the TSCA GLP Standards the requirements for testing facilities for the care of chemical or physical matrices (e.g., soil or water), plants, and microorganisms, as well as animals. Accordingly, the Agency is proposing to further modify § 792.43 by incorporating the term "test system" when facility requirements should extend beyond "animal" care.

b. Consistent with the Agency's intent to incorporate the environmental testing provisions currently found in Subpart L into Subparts A through J of Part 792, paragraphs (a)(1), (a)(2), (d), (e), (f), (g), and (h) in proposed § 792.43 have been added or modified to incorporate the provisions currently found in § 792.228(b) (1) through (7).

c. EPA proposes to modify § 792.43(a) to allow testing facilities to provide for isolation areas rather than quarantine areas. This change is consistent with the proposal to modify § 792.90(b) to allow "isolation" of newly received animals rather than requiring "quarantine" [See Unit I.D. of this preamble for a discussion of proposed § 792.90(b)].

d. In § 792.43(c), EPA proposes to delete the requirement that separate areas be provided in all cases for the diagnosis, treatment, and control of test system diseases. Instead, it is proposed that such separate areas be provided "as appropriate." This proposal is consistent with the September 4, 1987, revised FDA GLP regulations.

EPA has proposed this modification in order to allow laboratories the option of disposing of diseased animals and other test systems from the experiment without also bearing the expense of maintaining separate areas in testing facilities for diagnosis, treatment, and control of disease. Additionally, EPA recognizes that the diagnosis and treatment requirements of § 792.43(c) may not be appropriate when dealing with such test systems as soil, plants, or microorganisms. However, if the decision is made not to dispose of the test system from the study, then test system care facilities, as specified in proposed § 792.43(c), must be provided.

e. EPA proposes to conform to the revised FDA GLPs by deleting § 792.43(e) in its entirety. Currently, § 792.43(e) requires test system facilities to be designed, constructed, and located so as to minimize disturbances which may interfere with the study. EPA agrees with FDA that this provision is already adequately covered in § 792.41, which requires that facilities be of suitable size construction, and, for outdoor testing facilities, location to facilitate the proper conduct of the study.

7. *Section 792.45 Test system supply facilities.* a. EPA proposes to incorporate the provisions of § 792.228(c) into § 792.45. Therefore, proposed § 792.45 will require that supply facilities necessary for environmental testing be provided when appropriate.

b. Consistent with the proposed expanded scope of this section, EPA is also proposing to retitle § 792.45 from "Animal supply facilities" to "Test system supply facilities."

c. EPA proposes to modify § 792.45 to state "Perishable supplies shall be preserved by appropriate means." This change is being proposed to conform with the revised FDA GLPs and recognizes that there are a variety of acceptable storage and preservation procedures available other than refrigeration. Depending on the stability characteristics of the perishable material, acceptable storage and preservation methods may include desiccation, room temperature-low humidity, and constant temperature-low humidity.

d. EPA also proposes to delete the phrase "or feed" from the last sentence of § 792.45. Both EPA and FDA consider "feed" to be a "supply." Therefore, the use of the word "feed" in § 792.45 is redundant.

8. *Section 792.49 Laboratory operation areas.* a. EPA proposes to conform with FDA's revised GLP regulations by deleting paragraph (b) from § 792.49, adding the phrase "and specialized" after the word "routine" and before the word "procedures," and deleting the qualifying phrase "including specialized areas for performing activities such as aseptic surgery, intensive care, necropsy, histology, radiography, and handling of biohazardous materials."

Paragraphs (a) and (b), as currently worded, describe activities which require that separate laboratory space be provided. As FDA noted in its proposal to modify its corresponding section, the list of activities that currently appears in paragraphs (a) and (b) is not all inclusive and is not essential for the clarity of these sections. Further, by adding the phrase "and specialized," the proposed new paragraph will encompass all activities now listed in paragraphs (a) and (b).

b. In § 792.49, EPA proposes to add the phrase "and other space" after the words "laboratory space" and before the word "shall." As discussed in Unit I.C. of this preamble, this change to § 792.49 is being proposed to reflect that testing does not necessarily take place within the confines of a traditional indoor laboratory. Proposed § 792.49 would require that there be enough space provided to perform the procedures required by the protocol wherever testing takes place (i.e., indoor laboratory or field station).

9. *Section 792.53 Administrative and personnel facilities.* As in the revised FDA GLP regulations, EPA proposes to delete § 792.53 in its entirety. EPA agrees with FDA that the requirements of this section are not necessary for achieving the goals of the TSCA GLP standards.

10. *Section 792.61 Equipment design.* In § 792.61, EPA proposes to delete the phrase "Automatic, mechanical, or electronic" from the beginning of the first sentence. EPA agrees with FDA that the deletion of these qualifying terms provides for a more general interpretation of the word "equipment."

11. *Section 792.63 Maintenance and calibration of equipment.* a. Consistent with the FDA GLPs, EPA is proposing to amend § 792.63(b) to state that standard

operating procedures (SOPs) for remedial action for equipment, in the event of failure or malfunction of equipment, need only be established when "appropriate." This change acknowledges that laboratories may choose to discard rather than repair equipment, and in such cases SOPs which delineate remedial action are not necessary.

b. EPA is also proposing to conform to the revised FDA GLP regulations by deleting from § 792.63(b) the provision that copies of the SOPs shall be made available to laboratory personnel. EPA still believes that laboratory personnel must have access to laboratory SOPs; however, since this requirement is clearly stated in § 792.81(c), EPA considers the inclusion of this provision in § 792.63(b) to be redundant.

12. *Section 792.81 Standard operating procedures.* a. In § 792.81(b) (1), (2), (6), (7), (12), EPA is proposing to replace the word "animal" with the term "test system." As discussed previously in this preamble, this modification is consistent with the broad scope of test systems which may be used in environmental testing. Further, the Agency proposes to extend all the SOP requirements outlined by § 792.81 to environmental testing. For instance, the provisions of proposed § 792.81(b)(11), which require SOPs for the maintenance and calibration of equipment, would apply to procedures for preparation and maintenance of incubators, greenhouses, or growth chambers, currently required under § 792.228(d).

b. In § 792.81(b)(5), EPA is proposing to require that SOPs be established for tests wherever the testing is undertaken, including those conducted in the field. Accordingly, it is proposed that § 792.81(b)(5) read "Laboratory or other tests" (see discussion of "field testing" in Unit I.C. of this preamble).

c. In conformance with FDA's revised GLP regulations, EPA is proposing to delete the list of examples for laboratory manuals and SOPs required to be made immediately available under § 792.81(c). EPA still intends that laboratory areas must have immediately available manuals and SOPs for laboratory procedures being performed. This requirement still includes toxicology, histology, clinical chemistry, hematology, teratology, and necropsy, if applicable. However, this list is not all inclusive and is too broad to serve as a useful guide. For example, this requirement also includes SOPs for the maintenance, repair, and calibration of equipment as described in § 792.63(b).

d. EPA is also proposing to amend the language of § 792.81(c) to clarify that the requirement of this section also applies to field testing facilities. Therefore, it is proposed that § 792.81(c) will read, "Each laboratory *or other study* area shall have immediately available manuals and standard operating procedures relative to the laboratory or field procedures being performed."

13. *Section 792.90 Animal and other test system care.* a. EPA is proposing to retitle § 792.90 from "Animal care" to "Animal and other test system care." As previously stated, testing required by EPA may involve plants, soils, microorganisms, and other test systems, in addition to animals. The proposed title to § 792.90 reflects the broader scope of test systems for which the EPA intends this section to apply.

Further, it is proposed that the provisions for test system care for ecological effects testing, found in § 792.228(e), be incorporated into proposed § 792.90. Specifically, the proposed revision incorporates the requirements of: § 792.228(e)(1) into proposed § 792.90(b), § 792.228(e)(2) into proposed § 792.90(d), § 792.228(e)(3) into proposed § 792.90(e)(1), § 792.228(e)(4) into proposed § 792.90(f), § 792.228(e)(5) into proposed § 792.90(g), and § 792.228(e)(6) into proposed § 792.90(j).

b. EPA proposes to modify § 792.90(b) to provide for the evaluation of a test system's health status, or the appropriateness of the test system for the study, according to acceptable "scientific practice." This section, as proposed, will still require that newly received animals must have their health status evaluated according to acceptable veterinary medical practices. However, EPA recognizes that it may not be appropriate to evaluate the health status of certain test systems (e.g., soil or water) or to require that a plant, microorganism, soil, or water be evaluated according to acceptable veterinary medical practice to determine their appropriateness for a study. EPA is only concerned that test systems used in a study are free of any disease or condition which may interfere with the purpose or conduct of the study, and that the proper precautions, as stated in § 792.90(b), are taken to comply with this requirement.

c. Additionally, EPA is proposing to modify § 792.90(b), to require "isolation" rather than "quarantine" of newly received animals. This proposal is consistent with FDA's revision to its GLP regulations.

As previously stated, the intent of § 792.90(b) is to prevent the entry of unhealthy or inappropriate test systems into the study, as required by § 792.90(c). Currently, § 792.90(b) provides that this intent be achieved through "quarantine." However, the term "quarantine" suggests a rigid set of procedures, including a mandatory holding period, a specific list of diagnostic procedures, and the use of specialized facilities and test system care practices, which may be an unnecessary burden to industry.

EPA agrees with FDA's conclusion, discussed in the preamble to its revised GLP regulation (52 FR 33775; September 4, 1987), that isolation and evaluation of health status are sufficient precautions against contamination of test systems and, therefore, fulfill the intent of this section. FDA further states that such a revision would provide laboratories the flexibility to develop isolation and health status evaluation procedures best suited for the age, species, class, and type of the test system, as well as the type of study to be performed.

d. EPA proposes to conform to the FDA GLPs by modifying § 792.90(c) to require isolation of diseased test systems only when necessary.

Currently, § 792.90(c) requires that animals which contract a disease or condition shall be isolated in all cases. This requirement would in turn require that separate facilities be available for the isolation of these animals. However, as discussed in the proposal for § 792.43(c), both EPA and FDA believe that laboratories should be given flexibility in their disposition of diseased test systems. As FDA discussed in the proposed revisions to its GLP regulations (49 FR 43533; October 29, 1984), the proposed modification to § 792.90(c) will allow laboratories the option of: (1) Leaving the diseased test system in the experiment provided that the integrity of the study will not be adversely affected by this action; (2) disposing of the test system; or (3) isolating, treating, and returning the test system to the study.

14. *Section 792.105 Test, control, and reference substance characterization.* a. In revised 21 CFR 58.105(a), FDA has deleted the requirement that test and control substance characteristics shall be determined and documented for each batch "before the initiation of the study." This change has not been incorporated by EPA in its proposed revision to § 792.105(a). However, EPA proposes to modify § 792.105(a) to require that test, control, *or reference* substance characterization be determined and documented for each batch before its use in the experiment. EPA feels that this proposed requirement is necessary because it is essential that characteristics of test, control, and reference substances be known prior to their administration or use in an experiment.

EPA's recent experience with antimony trioxide has shown that extensive analytical work was necessary prior to test initiation. Certain assumptions regarding the product's characteristics were used in the protocols for antimony trioxide testing which proved invalid. These invalid assumptions necessitated modifications to the proposed study, resulting in the delay and rescheduling of other subsequent studies. If the analytical work had preceded the toxicology studies, the studies would not have failed and modifications to the studies woul d not have been necessary. The Agency's conclusion is that it is better to delay study schedules than to initiate improper experimental procedures which will produce invalid results.

b. FDA has modified 21 CFR 58.105(b) to provide for the determination of the stability of the test or control substance either before the initiation of the study or through periodic analysis of each batch according to written standard operating procedures. EPA has chosen not to adopt this approach in proposed § 792.105(b) because the Agency does not agree that stability can adequately be demonstrated by periodic analysis without initial evaluation.

Further, there are many studies required by EPA where solubility of the test, control, and reference substance is of critical importance, such as aquatic toxicity studies. Therefore, EPA is proposing that solubility of the test, control, and reference substance be determined before the experimental start date if knowledge of the solubility characteristics is relevant for the proper conduct of the experiment.

It is EPA's contention that both stability and solubility of the test, control, and reference substance need to be determined before the experimental start date in order to ensure proper handling and administration of the test substance to the test system. However, since the determination of the solubility of the test, control, and reference substance is not a requirement in FDA's GLP regulations, EPA is interested in receiving public comment on this issue.

15. *Section 792.113 Mixtures of substances with carriers.* a. FDA has modified 21 CFR 58.113(a)(2) to require determination of the stability of the test and control substance in a mixture, as required by the conditions of the study, either before the initiation of the study or through periodic analysis of each batch. While EPA does not propose to modify § 792.113(a)(2) to provide the option of determining the stability of the mixture either before study initiation or through periodic analysis (see discussion for § 792.105(b)), EPA will modify this section to require stability testing only to the extent required by the conditions of the experiment. As proposed for § 792.105(b), EPA is also proposing to require that, when appropriate to the conduct of the experiment, solubility of the test, control, or reference substance in the mixture must be determined in the same manner (see discussion for § 792.105(b)). Additionally, as proposed for § 792.105 (a) and (b), EPA is proposing to replace the phrase "before the initiation of the study" with the phrase "before the experimental start date" (see discussion for § 792.105(a)).

The phrase "as required by the conditions of the experiment" has been added in order to clarify that determination of stability and, if appropriate, solubility of a test, control, or reference substance in a mixture is only necessary to support its actual time of use in the experiment. Therefore, it is not necessary to provide data which illustrate long-term stability of a mixture when the actual time that the mixture is used is short-term. For example, a test, control, or reference substance in a mixture that will be used the same day it is prepared will only require data sufficient to show stability and, if appropriate, solubility for 1 day.

b. Additionally, EPA proposes to incorporate into § 792.113(a)(2), the provision currently found in § 792.228(f)(2), which states that the determination of the stability or solubility of the test, control, or reference substance in the mixture must be done under the environmental conditions specified in the protocol.

c. EPA proposes to add new paragraph (c) to § 792.113 which incorporates the provisions of § 792.228(f)(3).

16. *Section 792.120 Protocol.* a. In 21 CFR 58.120(a), FDA has replaced the qualifying phrase "but shall not necessarily be limited to" with the phrase "as applicable." EPA proposes to adopt FDA's approach with some modifications. It is proposed that the phrase "Where applicable" appear before the information specified in § 792.120(a)(9), and continue to appear before the information required by § 792.120(a)(6). The phrase "but shall not necessarily be limited to" would remain in this section.

In FDA's discussion of this proposal (49 FR 43533; October 29, 1984), concerns were expressed that some of the information required to appear in the protocol is not applicable to all types of testing. Specifically, FDA points to the information required by 21 CFR 58.120(a) (9) and (11). In 21 CFR 58.120, paragraph (a)(9) requires a description of the diet used in a study as well as solvents, emulsifiers, and/or other materials used to solubilize or suspend the test or control substance before mixing with the carrier. FDA points out that this requirement is not applicable to radiation-emitting products. Section 58.120(a)(11) specifies that the protocol shall specify dosage level, and this requirement is not applicable to implantable medical devices.

Clearly, the basis for FDA's change is to accommodate concerns that are specific to the types of testing required by FDA and do not necessarily apply to testing required by EPA. Further, EPA is concerned that placing the phrase "as applicable" in § 792.120(a) suggests that there may be cases where it is not applicable for any of the other information required by § 792.120(a) to appear in the protocol. Therefore, the phrase "as applicable" should only appear before those items which are not necessarily appropriate to appear in the protocol for certain types of testing.

For example, there may be testing required by EPA where it may not be appropriate to require a protocol to contain the information specified in § 792.120(a)(9), such as describing and/or identifying the diet of a human subject involved in exposure testing. Therefore, EPA proposes to add the phrase "Where applicable" before the information specified in proposed § 792.120(a)(9).

b. In 21 CFR 58.120(a)(4), FDA has deleted the requirement that the protocol contain "The proposed starting and completion dates." EPA is proposing to retain this requirement in § 792.120(a)(4), but is proposing to modify this paragraph to require, "The proposed experimental start and termination dates."

EPA believes that this information is necessary for the evaluation of a protocol and the Agency's scheduling of additional related studies and audit reviews. Section 792.120(a)(4) is related to the selected study method, laboratory, and specialist availability, and other Agency and industry priorities. Often a group of experiments are carried out in sequence, so that both start and termination dates affect subsequent study expectations and timetables. Projected experimental start and termination dates identify the normal duration for a given experiment type and reflect any special considerations that may be unique to a laboratory, anticipated analytical or methodology work, and available resources, and it may also affect pending regulatory timetables.

Given that there are hundreds of studies that EPA must track, these estimated schedules, combined with those from other studies, allow the Agency to more efficiently schedule audits and regulatory action. Further considerations are the following: (1) The availability of composite schedules for many studies may be necessary to set realistic regulatory action goals; (2) composite study schedules are evaluated to schedule audits while several studies are ongoing or recently completed, and which may all be at a given laboratory or geographic location. This directly reduces EPA resources necessary for audit and regulatory review functions; and (3) standard business management by objectives requires intermediate calendar goals when scheduling multiple outputs, or a long-term single product. The master on-site laboratory schedule will incorporate these dates to carry out the study.

In 21 CFR 58.120(a)(5), FDA has deleted the requirement that the protocol contain a justification for the selection of the test system. EPA has chosen to retain this requirement in proposed § 792.120(a)(5).

Environmental studies, including both ecological effects and chemical fate, are more diverse than health effects testing. Further, details relevant to the test system design are more chemically dependent in the case of environmental effects and chemical fate testing than in the case of health effects testing. Many of the test systems in environmental studies must be modified in accordance with specific chemical characteristics. Therefore, EPA must allow a much broader range of flexibility in the nature of tests and selection of test systems. In order to fully understand the test and its results, EPA needs to have a discussion of the reasons for selection of the test system. In addition, EPA recognizes that industry may be engaged in state-of-the-art environmental testing. Under proposed § 792.120(a)(5), EPA can keep abreast of industry advances in such testing and ensure that their use of test systems is appropriate. EPA is interested in receiving public comment on whether to limit the requirement that the protocol contain a justification of the test system to environmental testing.

d. FDA has deleted from 21 CFR 58.120(a)(10) the requirement that the protocol include the route of administration and the reason for its choice. EPA has chosen to retain this requirement in proposed § 792.120(a)(10).

The chemicals regulated by FDA will usually have a predefined route of exposure. Therefore, it makes sense for FDA to eliminate the requirement to stipulate the route of administration and the reason for its choice within the protocol. Unlike FDA, EPA is concerned with presence in or exposure to various media (i.e., air, water, soil, sediment, chemicals, etc.) and may not know in advance the routes of exposure for the chemicals it regulates. Most chemicals and products regulated by EPA do not have set routes of exposure and may even have multiple routes of exposure. Therefore, EPA must consider a wide range of possible exposure routes in its regulatory decisions. Further, the route of administration is essential to determine the effectiveness of a test system for the purposes of a specific toxicology study. The route of administration affects the real dosage rates, and therefore, affects whether the impact of the exposure of the test substance is acute or chronic.

Therefore, EPA believes that, for its purposes, it is essential that the protocol contain the route of administration and the reason for its choice. This requirement will therefore remain in the EPA's TSCA GLP standards in § 792.120(a)(10).

e. EPA proposes to delete current § 792.120(a)(12) in its entirety. Currently, § 792.120(a)(12) requires that the protocol contain the method by which the degree of absorption of the test and control substance by the test system will be determined. EPA agrees with FDA's conclusion that this requirement is not necessary in the protocol.

f. In proposed § 792.120(a)(14), redesignated from current paragraph (a)(15), EPA proposes to conform with FDA's revised GLP regulations and require that the study director's signature be dated on the protocol.

EPA is proposing in § 792.3 that the study initiation date be defined as the date the protocol is signed by the study director. It is through the proposed requirement of § 792.120(a)(14), that the Agency will be able to identify the official study initiation date.

17. *Section 792.130 Conduct of a study.* a. FDA has modified 21 CFR 58.130(d) to provide that records of gross findings for a specimen from postmortem observations "should" be made available to the pathologist when examining that specimen's histopathology. EPA has chosen to retain the requirement that these records "shall," in all cases, be provided to a pathologist during study of the specimen.

EPA agrees with FDA's conclusion that for most studies it is important for the pathologist to have the records of gross findings available when examining a specimen histopathologically. However, it is FDA's contention that replacing the word "shall" with the word "should" will allow the histopathological evaluation of specimens in a "blind" fashion. EPA also recognizes that it may be appropriate for some studies to provide for "blinding" in histopathological evaluation. However, EPA maintains that, when specified by the protocol, the pathologist can accomplish "blinding," without violating § 792.130 by not looking at the records which have been provided. Therefore, it will remain EPA's requirement that the pathologist must have access to the records of gross findings when examining a specimen histopathologically.

b. In conformance with the revised FDA GLP regulations, in § 792.130(e), EPA proposes to replace the terms "computer" and "computer driven" with the term "automated data collection." EPA agrees with FDA that the terms "computer" or "computer driven" do not adequately reflect the data collection and storage technologies currently used by testing facilities. The Agency believes that the proposed term "automated data collection" provides a more appropriate description of the data collection and storage systems available for industry use.

18. *Section 792.135 Physical and chemical characterization studies.* EPA proposes to add § 792.135 in order to specify the provisions of the proposed TSCA GLP standards which will not apply to studies designed to determine the physical and chemical characteristics of a test, control, or reference substance. Most studies designed to determine the physical or chemical characteristics of a test, control, or reference substance rarely involve any modifications to the protocol or experimental design and are usually conducted in an assembly line fashion. Therefore, proposed § 792.135(a) relaxes the requirements of the GLP standards without compromising the quality or integrity of data generated from these studies.

However, in § 792.135(b), EPA is also proposing that the exemptions listed in proposed § 792.135(a) will not apply to studies designed to determine solubility, octanol water partition coefficient, volatility, and persistence of a test, control, or reference substance. These types of physical and chemical characterization studies are more complex in design, execution, and interpretation, and EPA does not believe that it can be assured of the quality and integrity of data generated from these studies without complete GLP compliance.

19. *Section 792.185 Reporting of study results.* In § 792.185(a)(5), EPA is proposing to require that the final report include information relating to the solubility, in addition to stability, of the test, control, or reference substance, if solubility information was important to the conduct of the experiment. This change is consistent with the proposed modifications to §§ 792.105(b) and 792.113(a)(2) (see the preamble discussion of proposed §§ 792.105(b) and 792.113(a)(2)).

20. *Section 792.190 Storage and retrieval of records and data.* a. In § 792.190(a), EPA proposes to conform to the revised FDA GLP regulations by modifying this section to state that specimens obtained from mutagenicity tests and specimens of blood, urine, feces, and biological fluids generated as a result of a study need *not* be retained. EPA is also proposing that § 792.190(a) state that specimens of soil, water, and plants obtained from environmental testing need *not* be retained. EPA agrees with FDA's conclusion that retention of these specimens beyond initial evaluation is burdensome and does not have a significant impact on the quality of a study.

b. As in the revised FDA GLPs, EPA proposes to revise § 792.190(e) by deleting the requirement that study materials which are retained in archives must be indexed specifically by test substance, date of study, test system, and nature of study. EPA agrees with FDA that the intent of this section is to require indexing of materials in such a way as to permit expedient retrieval from archives. EPA does not believe it is necessary to stipulate the specific indexing terms which must be used.

21. *Section 792.195 Retention of records.* a. EPA proposes to delete paragraphs (b)(2) and (3) of § 792.195, redesignate paragraph (b)(1) as (b), and amend paragraph (b) to require a retention period for documentation records, raw data, and specimens of 5 years from the date the results of any study are submitted to the Agency.

Currently, § 792.195(b) requires a retention period for records, raw data, and specimens under paragraph (b)(1) of 10 years following the effective date of the applicable final test rule and, under paragraph (b)(2) of 10 years following the publication date of the acceptance of a negotiated test agreement. This section also recommends a retention period for such materials of 5 years following the date studies are submitted to the Agency under TSCA section 5.

As stated in the preamble to the 1983 TSCA GLP regulation (48 FR 53935; November 29, 1983), EPA believes that it is essential that study records, raw data, and specimens be maintained to provide the Agency with a sufficient period of time to review the study results and implement any appropriate regulatory actions. Further, it is essential that records, raw data, and specimens be available to suppport Agency decisions in case of court challenges to those decisions. However, the Agency sees no reason to vary record retention requirements and has concluded that a record retention period of 5 years from the date the study is submitted to EPA is a sufficient period of time to meet the Agency concerns and goals. Finally, the record retention period proposed in § 792.195(b) is preferable to the timeframes currently required because it is consistent with the requirements currently set forth in the FIFRA GLPs, in 40 CFR 160.195(b)(2), and the FDA Good Laboratory Practice regulations in 21 CFR 58.195(b).

b. In § 792.195, EPA proposes to delete the examples provided in the first sentence of paragraph (c). EPA has proposed this change in conformity with FDA's recent revision because EPA agrees with FDA that these examples do not clarify which materials must be retained from a study and, therefore, are not necessary in this section.

c. EPA is also proposing to modify § 792.195(c) to state that specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, biological fluids, do not need to be retained beyond quality assurance review. This change has been adopted in order to be consistent with the change discussed in proposed § 792.190(a).

d. In new § 792.195(i), EPA proposes to allow records and other "raw data" required by these regulations to be retained either as original records or as true copies, such as photocopies, microfiche, or other accurate reproductions of the original records. This provision would be incorporated in the TSCA GLPs in § 792.195(i) in order to be consistent with the changes to FDA's Good Laboratory Practice regulations.

II. Economic Analysis

The proposal to expand coverage of the TSCA GLP standards to testing conducted in the field is not expected to increase testing costs significantly. Further, the revisions to the TSCA GLP standards which reflect the FDA GLP revisions primarily provide relief from the original GLP standards (ICF 1987). Therefore, these amendments to the TSCA GLPs are not expected to have a significant economic impact on testing under TSCA.

III. Other Regulatory Requirements

A. Executive Order 12291

Under Executive Order 12291, EPA is required to judge whether a rule is a "major" one and is therefore subject to the requirement of a Regulatory Impact Analysis. The proposed amendments of the TSCA Good Laboratory Practice Standards would not be a major rule because they do not meet any of the criteria set forth and defined in section 1(b) of the Order.

B. Regulatory Flexibility Act

The proposed amendments to the TSCA GLP standards are not expected to have a significant impact on a substantial number of small businesses since little or no economic impact is expected from the revision overall.

C. Paperwork Reduction Act

The Office of Management and Budget (OMB) has approved the information collection requirements contained in this proposed rule under the provisions of the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.* and has assigned OMB control number 2070-0033. Comments on these requirements should be submitted to the Office of Information and Regulatory Affairs of OMB, marked "Attention: Desk Officer for EPA." The final rule will respond to any OMB or public comments on the information collection requirements.

List of Subjects in 40 CFR Part 792

Good laboratory practices, Laboratories, Environmental protection, Hazardous materials, Chemicals, Recordkeeping and reporting requirements.

Dated: December 8, 1987.

Lee M. Thomas,

Administrator.

Therefore, it is proposed that 40 CFR Part 792 be amended as follows:

PART 792—[AMENDED]

1. The authority citation for Part 792 is revised to read as follows:

Authority: 15 U.S.C. 2603.

2. In § 792.1, by revising paragraphs (a) and (c) to read as follows:

§ 792.1 Scope.

(a) This part prescribes good laboratory practices for conducting studies relating to health effects, environmental effects, and chemical fate testing. This part is intended to ensure the quality and integrity of data submitted pursuant to testing consent agreements and test rules issued under section 4 of the Toxic Substances

Control Act (TSCA) (Pub. L. 94–469, 90 Stat. 2006, 15 U.S.C. 2603 et seq.).

* * * * *

(c) It is the Agency's policy that all data developed under section 5 of TSCA be in accordance with provisions of this part. If data are not developed in accordance with the provisions of this part, the Agency will consider such data insufficient to evaluate the health and environmental effects of the chemical substances unless the submitter provides additional information demonstrating that the data are reliable and adequate.

3. In § 792.3, by removing the alphabetical paragraph designations in paragraphs (a) through (q); by revising the definitions for "Control substance", "Study," and "Test system"; by replacing the term "Test substance or mixture" with "Test substance"; by amending the definition for "Sponsor" by revising paragraph (2) thereunder; and by adding and alphabetically inserting definitions for "Carrier", "Experimental start date", "Experimental termination date", "Reference substance", "Study completion date", "Study initiation date", and "Vehicle", to read as follows:

§ 792.3 Definitions.

* * * * *

"Carrier" means any material (e.g., feed, water, soil, nutrient media) with which the test substance is combined for administration to test organisms.

"Control substance" means any chemical substance or mixture or any other material other than a test substance, feed, or water that is administered to the test system in the course of study for the purpose of establishing a basis for comparison with the test substance for no effect levels.

* * * * *

"Experimental start date" means the first date the test substance is applied to the test system.

"Experimental termination date" means the last date on which data are collected directly from the study.

* * * * *

"Reference substance" means any chemical substance or mixture or material other than a test substance, feed, or water that is administered to or used in analyzing the test system in the course of a study for purposes of establishing a basis for comparison with the test substance for known effect levels.

* * * * *

"Sponsor" means:

* * * * *

(2) A person who submits a study to the EPA in response to a TSCA section 4(a) test rule and/or a person who submits a study under a TSCA section 4 testing consent agreement or a TSCA section 5 rule or order to the extent the agreement, rule or order references this part; or

* * * * *

"Study" means any experiment in which a test substance is studied in a test system under laboratory conditions or in the environment to determine or help predict its effects, metabolism, environmental and chemical fate, persistence, or other characteristics in humans, other living organisms, or media. The term does not include basic exploratory studies carried out to determine whether a test substance has any potential utility.

"Study completion date" means the date the final report is signed by the study director.

* * * * *

"Study initiation date" means the date the protocol is signed by the study director.

* * * * *

"Test substance" means a substance or mixture administered or added to a test system in a study, which substance or mixture is used to develop data to meet the requirements of a TSCA section 4(a) test rule and/or is developed under a TSCA section 4 testing consent agreement or section 5 rule or order to the extent the agreement, rule or order references this part.

"Test system" means any animal, plant, microorganism, chemical or physical matrix (e.g., soil or water), or subparts thereof, to which the test, control, or reference substance is administered or added for study. "Test system" also includes appropriate groups or components of the system not treated with the test, control, or reference substance.

* * * * *

"Vehicle" means any agent which facilitates the mixture, dispersion, or solubilization of a test substance with a carrier.

4. In § 792.12, by revising the introductory text to read as follows:

§ 792.12 Statement of compliance or non-compliance.

Any person who submits to EPA a test required by a testing consent agreement or a test rule issued under section 4 of TSCA shall include in the submission a true and correct statement, signed by the sponsor and the study director, of one of the following types:

* * * * *

5. In § 792.17, by revising the introductory text of paragraph (a) and paragraph (c) to read as follows:

§ 792.17 Effects of non-compliance.

(a) The sponsor or any other person who is conducting or has conducted a test to fulfill the requirements of a testing consent agreement or a test rule issued under section 4 of TSCA will be in violation of section 15 of TSCA if:

* * * * *

(c) If data submitted to fulfill a requirement of a testing consent agreement or a test rule issued under section 4 of TSCA are not developed in accordance with this part, EPA may determine that the sponsor has not fulfilled its obligations under section 4 of TSCA and may require the sponsor to develop data in accordance with the requirements of this part in order to satisfy such obligations.

6. In § 792.29, by revising paragraphs (d), (e), and (f) to read as follows:

§ 792.29 Personnel.

* * * * *

(d) Personnel shall take necessary personal sanitation and health precautions designed to avoid contamination of test, control, and reference substances and test systems.

(e) Personnel engaged in a study shall wear clothing appropriate for the duties they perform. Such clothing shall be changed as often as necessary to prevent microbiological, radiological, or chemical contamination of test systems and test, control, and reference substances.

(f) Any individual found at any time to have an illness that may adversely affect the quality and integrity of the study shall be excluded from direct contact with test systems, test, control, and reference substances and any other operation or function that may adversely affect the study until the condition is corrected. All personnel shall be instructed to report to their immediate supervisors any health or medical conditions that may reasonably be considered to have an adverse effect on a study.

7. In § 792.31, by revising paragraph (b) to read as follows:

§ 792.31 Testing facility management.

* * * * *

(b) Replace the study director promptly if it becomes necessary to do so during the conduct of a study.

* * * * *

8. In § 792.35, by revising paragraphs (a) and (b) (1) and (3) and removing paragraph (e) to read as follows:

§ 792.35 Quality assurance unit.

(a) A testing facility shall have a quality assurance unit which shall be responsible for monitoring each study to assure management that the facilities, equipment, personnel, methods, practices, records, and controls are in conformance with the regulations in this part. For any given study, the quality assurance unit shall be entirely separate from and independent of the personnel engaged in the direction and conduct of that study.

(b) * * *

(1) Maintain a copy of a master schedule sheet of all studies conducted at the testing facility indexed by test substance and containing the test system, nature of study, date study was initiated, current status of each study, identity of the sponsor, and name of the study director.

* * * * *

(3) Inspect each study at intervals adequate to ensure the integrity of the study and maintain written and properly signed records of each periodic inspection showing the date of the inspection, the study inspected, the phase or segment of the study inspected, the person performing the inspection, findings and problems, action recommended and taken to resolve existing problems, and any scheduled date for re-inspection. Any problems which are likely to affect study integrity found during the course of an inspection shall be brought to the attention of the study director and management immediately.

* * * * *

9. By revising § 792.41 to read as follows:

§ 792.41 General.

Each testing facility shall be of suitable size and construction to facilitate the proper conduct of studies. Testing facilities which are not located within an indoor controlled environment shall be of suitable location to facilitate the proper conduct of studies. Testing facilities shall be designed so that there is a degree of separation that will prevent any function or activity from having an adverse effect on the study.

10. By revising § 792.43 to read as follows:

§ 792.43 Test system care facilities.

(a) A testing facility shall have a sufficient number of animal rooms or other test system areas, as needed, to ensure: proper separation of species or test systems, isolation of individual projects, quarantine or isolation of animals or other test systems, and routine or specialized housing of animals or other test systems.

(1) In tests with plants or aquatic animals, proper separation of species can be accomplished within a room or area by housing them separately in different chambers or aquaria. Separation of species is unnecessary where the protocol specifies the simultaneous exposure of two or more species in the same chamber, aquarium, or housing unit.

(2) Aquatic toxicity tests for individual projects shall be isolated to the extent necessary to prevent cross-contamination of different chemicals used in different tests.

(b) A testing facility shall have a number of animal rooms or other test system areas separate from those described in paragraph (a) of this section to ensure isolation of studies being done with test systems or test, control, and reference substances known to be biohazardous, including volatile substances, aerosols, radioactive materials, and infectious agents.

(c) Separate areas shall be provided, as appropriate, for the diagnosis, treatment, and control of laboratory test system diseases. These areas shall provide effective isolation for the housing of test systems either known or suspected of being diseased, or of being carriers of disease, from other test systems.

(d) Facilities shall have proper provisions for collection and disposal of contaminated water, soil, or other spent materials. When animals are housed, facilities shall exist for the collection and disposal of all animal waste and refuse or for safe sanitary storage of waste before removal from the testing facility. Disposal facilities shall be so provided and operated as to minimize vermin infestation, odors, disease hazards, and environmental contamination.

(e) Facilities shall have provisions to regulate environmental conditions (e.g., temperature, humidity, photoperiod) as specified in the protocol.

(f) For marine test organisms, an adequate supply of clean sea water or artificial sea water (prepared from deionized or distilled water and sea salt mixture) shall be available. The ranges of composition shall be as specified in the protocol.

(g) For freshwater organisms, an adequate supply of clean water of the appropriate hardness, pH, and temperature, and free of contaminants capable of interfering with the study shall be available as specified in the protocol.

(h) For plants, an adequate supply of soil of the appropriate composition, as specified in the protocol, shall be available as needed.

11. By revising § 792.45 to read as follows:

§ 792.45 Test system supply facilities.

(a) There shall be storage areas, as needed, for feed, nutrients, soils, bedding, supplies, and equipment. Storage areas for feed, nutrients, soils, and bedding shall be separated from areas housing the test systems and shall be protected against infestation or contamination. Perishable supplies shall be preserved by appropriate means.

(b) When appropriate, plant supply facilities shall be provided. These include:

(1) Facilities, as specified in the protocol, for holding, culturing, and maintaining algae and aquatic plants.

(2) Facilities, as specified in the protocol, for plant growth (e.g., greenhouses, growth chambers, light banks).

(c) When appropriate, facilities for aquatic animal tests shall be provided. These include aquaria, holding tanks, ponds, and ancillary equipment, as specified in the protocol.

12. By revising § 792.47 to read as follows:

§ 792.47 Facilities for handling test, control, and reference substances.

(a) As necessary to prevent contamination or mixups, there shall be separate areas for:

(1) Receipt and storage of the test, control, and reference substances.

(2) Mixing of the test, control, and reference substances with a carrier, e.g., feed.

(3) Storage of the test, control, and reference substance mixtures.

(b) Storage areas for test, control, and/or reference substance and for test, control, and/or reference mixtures shall be separate from areas housing the test systems and shall be adequate to preserve the identity, strength, purity, and stability of the substances and mixtures.

13. By revising § 792.49 to read as follows:

§ 792.49 Laboratory operation areas.

Separate laboratory space and other space shall be provided, as needed, for the performance of the routine and specialized procedures required by studies.

§ 792.53 [Removed]

14. By removing § 792.53 *Administrative and personnel facilities.*

15. By revising § 792.61 to read as follows:

§ 792.61 Equipment design.

Equipment used in the generation, measurement, or assessment of data and equipment used for facility environmental control shall be of appropriate design and adequate capacity to function according to protocol and shall be suitably located for operation, inspection, cleaning, and maintenance.

16. In § 792.63, by revising paragraph (b) to read as follows:

§ 792.63 Maintenance and calibration of equipment.

* * * * *

(b) The written standard operating procedures required under § 792.81(b)(11) shall set forth in sufficient detail the methods, materials, and schedules to be used in the routine inspection, cleaning, maintenance, testing, calibration, and/or standardization of equipment, and shall specify when appropriate, remedial action to be taken in the event of failure or malfunction of equipment. The persons responsible for the standard operating procedures shall designate the person responsible for the performance of each operation.

* * * *

17. In § 792.81, by revising paragraphs (b) (1), (2), (3), (5), (6), (7), and (12) and (c) to read as follows:

§ 792.81 Standard operating procedures.

* * * * *

(b) * * *

(1) Test system room preparation.

(2) Test system care.

(3) Receipt, identification, storage, handling, mixing, and method of sampling of the test, control, and reference substances.

* * * * *

(5) Laboratory or other tests.

(6) Handling of test systems found moribund or dead during study.

(7) Necropsy of test systems or postmortem examination of test systems.

* * * * *

(12) Transfer, proper placement, and identification of test systems.

(c) Each laboratory or other study area shall have immediately available manuals and standard operating procedures relative to the laboratory or field procedures being performed. Published literature may be used as a supplement to standard operating procedures.

* * * * *

18. By revising § 792.90 to read as follows

§ 792.90 Animal and other test system care.

(a) There shall be standard operating procedures for the housing, feeding, handling, and care of animals and other test systems.

(b) All newly received test systems from outside sources shall be isolated and their health status or appropriateness for the study evaluated. This evaluation shall be in accordance with acceptable veterinary medical practice or scientific practice.

(c) At the initiation of a study, test systems shall be free of any disease or condition that might interfere with the purpose or conduct of the study. If during the course of the study, the test systems contract such a disease or condition, the diseased test systems should be isolated, if necessary. These test systems may be treated for disease or signs of disease provided that such treatment does not interfere with the study. The diagnosis, authorization of treatment, description of treatment, and each date of treatment shall be documented and shall be retained.

(d) Warm-blooded animals, adult reptiles, and adult terrestrial amphibians used in laboratory procedures that require manipulations and observations over an extended period of time, such as studies that require these test systems to be removed from and returned to their test system-housing units for any reason (e.g., cage cleaning, treatment, etc.), shall receive appropriate identification (e.g., tattoo, toe clip, color code, ear tag, ear punch, etc.). All information needed to specifically identify each test system within the test system-housing unit shall appear on the outside of that unit. Suckling mammals and juvenile birds are excluded from the requirement of individual identification unless otherwise specified in the protocol.

(e) Except as specified in paragraph (e)(1) of this section, test systems of different species shall be housed in separate rooms when necessary. Test systems of the same species, but used in different studies, should not ordinarily be housed in the same room when inadvertent exposure to test, control, or reference substances or test system mixup could affect the outcome of either study. If such mixed housing is necessary, adequate differentiation by space and identification shall be made.

(1) Plants, invertebrate animals, aquatic vertebrate animals, and organisms that may be used in multispecies tests need not be housed in separate rooms, provided that they are adequately segregated to avoid mixup and cross contamination.

(2) [Reserved]

(f) Cages, racks, pens, enclosures, aquaria, holding tanks, ponds, growth chambers, and other holding, rearing, and breeding areas, and accessory equipment, shall be cleaned and sanitized at appropriate intervals.

(g) Feed, soil, and water used for the test systems shall be analyzed periodically to ensure that contaminants known to be capable of interfering with the study and reasonably expected to be present in such feed, soil, or water are not present at levels above those specified in the protocol. Documentation of such analyses shall be maintained as raw data.

(h) Bedding used in animal cages or pens shall not interfere with the purpose or conduct of the study and shall be changed as often as necessary to keep the animals dry and clean.

(i) If any pest control materials are used, the use shall be documented. Cleaning and pest control materials that interfere with the study shall not be used.

(j) All plant and animal test organisms shall be acclimatized, prior to their use in an experiment, to the environmental conditions of the test.

Subpart F—Test, Control, and Reference Substances

19. By revising the heading for Subpart F to read as set forth above.

20. By revising § 792.105 to read as follows:

§ 792.105 Test, control and reference substance characterization.

(a) The identity, strength, purity, and composition, or other characteristics which will appropriately define the test, control, or reference substance shall be determined for each batch and shall be documented before its use in an experiment. Methods of synthesis, fabrication, or derivation of the test, control, or reference substance shall be documented by the sponsor or the testing facility.

(b) The stability and, when relevant to the conduct of the experiment, the solubility of each test, control, or reference substance shall be determined by the testing facility or by the sponsor before the experimental start date. Where periodic analysis of each batch is required by the protocol, there shall be written standard operating procedures that shall be followed.

(c) Each storage container for a test, control, or reference substance shall be labeled by name, chemical abstracts service number (CAS) or code number, batch number, expiration date, if any, and, where appropriate, storage conditions necessary to maintain the

identity, strength, purity, and composition of the test, control, or reference substance. Storage containers shall be assigned to a particular test substance for the duration of the study.

(d) For studies of more than 4 weeks' duration, reserve samples from each batch of test, control, and reference substances shall be retained for the period of time provided by § 792.195.

(e) The stability of test, control, and reference substances under test conditions shall be known for all studies.

21. In § 792.107, by revising the section heading and introductory text to read as follows:

§ 792.107 Test, control, and reference substance handling.

Procedures shall be established for a system for the handling of the test, control, and reference substances to ensure that:

* * * * *

22. By revising § 792.113 to read as follows:

§ 792.113 Mixtures of substances with carriers.

(a) For each test, control, or reference substance that is mixed with a carrier, tests by appropriate analytical methods shall be conducted:

(1) To determine the uniformity of the mixture and to determine, periodically, the concentration of the test, control, or reference substance in the mixture.

(2) To determine the stability and, when relevant to the conduct of the experiment, the solubility of the test, control, or reference substance in the mixture, before the experimental start date. Determination of the stability and solubility of the test, control, or reference substance in the mixture shall be done under the environmental conditions specified in the protocol and as required by the conditions of the experiment. Where periodic analysis of the mixture is required by the protocol, there shall be written standard operating procedures that shall be followed.

(b) Where any of the components of the test, control, or reference substance carrier mixture has an expiration date, that date shall be clearly shown on the container. If more than one component has an expiration date, the earliest date shall be shown.

(c) If a vehicle is used to facilitate the mixing of a test substance with a carrier, assurance shall be provided that the vehicle does not interfere with the integrity of the test.

23. In § 792.120, by revising paragraph (a) to read as follows:

§ 792.120 Protocol.

(a) Each study shall have an approved written protocol that clearly indicates the objectives and all methods for the conduct of the study. The protocol shall contain but shall not necessarily be limited to the following information:

(1) A descriptive title and statement of the purpose of the study.

(2) Identification of the test, control, and reference substance by name, chemical abstracts service (CAS) number or code number.

(3) The name and address of the sponsor and the name and address of the testing facility at which the study is being conducted.

(4) The proposed experimental start and termination dates.

(5) Justification for selection of the test system.

(6) Where applicable, the number, body weight, sex, source of supply, species, strain, substrain, and age of the test system.

(7) The procedure for identification of the test system.

(8) A description of the experimental design, including methods for the control of bias.

(9) Where applicable, a description and/or identification of the diet used in the study as well as solvents, emulsifiers and/or other materials used to solubilize or suspend the test, control, or reference substances before mixing with the carrier. The description shall include specifications for acceptable levels of contaminants that are reasonably expected to be present in the dietary materials and are known to be capable of interfering with the purpose or conduct of the study if present at levels greater than established by the specifications.

(10) The route of administration and the reason for its choice.

(11) Each dosage level, expressed in milligrams per kilogram of body or test system weight or other appropriate units, of the test, control, or reference substance to be administered and the method of frequency of administration.

(12) The type and frequency of test analyses, and measurements to be made.

(13) The records to be maintained.

(14) The date of approval of the protocol by the sponsor and the dated signature of the study director.

(15) A statement of the proposed statistical method.

* * * * *

24. In § 792.130, by revising paragraphs (d) and (e) to read as follows:

§ 792.130 Conduct of a study.

* * * * *

(d) In animal studies where histopathology is required, records of gross findings for a specimen from postmortem observations shall be available to a pathologist when examining that specimen histopathologically.

(e) All data generated during the conduct of a study, except those that are generated by automated data collection systems, shall be recorded directly, promptly, and legibly in ink. All data entries shall be dated on the day of entry and signed or initialed by the person entering the data. Any change in entries shall be made so as not to obscure the original entry, shall indicate the reason for such change, and shall be dated and signed or identified at the time of the change. In automated data collection systems, the individual responsible for direct data input shall be identified at the time of data input. Any change in automated data entries shall be made so as not to obscure the original entry, shall indicate the reason for change, shall be dated, and the responsible individual shall be identified.

25. By adding § 792.135 to read as follows:

§ 792.135 Physical and chemical characterization studies.

(a) Except as provided in paragraph (b) of this section, the following provisions shall not apply to studies designed to determine physical and chemical characteristics of a test, control, or reference substance:

§ 792.31 (c), (d), and (g)
§ 792.35 (b) and (c)
§ 792.43
§ 792.45
§ 792.47
§ 792.49
§ 792.81(b) (1), (2), (6) through (9), and (12)
§ 792.90
§ 792.105 (a) through (d)
§ 792.113
§ 792.120(a) (5) through (12), and (15)
§ 792.185(a) (5) through (8), (10), (12), and (14)
§ 792.195 (c) and (d).

(b) The exemptions provided in paragraph (a) of this section shall not apply to physical/chemical characterization studies designed to determine solubility, octanol water partition coefficient, volatility, and persistence (such as biodegradation, photodegradation, and chemical degradation studies), and such studies shall be conducted in accordance with this part.

26. In § 792.185, by revising paragraphs (a) (4) and (5) to read as follows:

§ 792.185 Reporting of study results.

(a) * * *

(13) The test, control, and reference substances identified by name, chemical abstracts service (CAS) number or code number, strength, purity, and composition or other appropriate characteristics.

[illegible]ility and, when relevant to the [illegible] the experiment, the solubility [illegible], control, and reference substances under the conditions of administration.

* * * * *

27. In § 792.190, by revising paragraphs (a) and (e) to read as follows:

§ 792.190 Storage and retrieval of records and data.

(a) All raw data, documentation, records, protocols, specimens, and final reports generated as a result of a study shall be retained. Specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, and biological fluids, do not need to be retained beyond quality assurance review. Correspondence and other documents relating to interpretation and evaluation of data, other than those documents contained in the final report, also shall be retained.

* * * * *

(e) Material retained or referred to in the archives shall be indexed to permit expedient retrieval.

28. In § 792.195, by revising paragraphs (b) and (c), and adding paragraph (i), to read as follows:

§ 792.195 Retention of records.

* * * * *

(b) Except as provided in paragraph (c) of this section, documentation records, raw data, and specimens pertaining to a study and required to be retained by this part shall be retained in the archive(s) for a period of at least 5 years following the date on which the results of the study are submitted to EPA.

(c) Wet specimens, samples of test, control, or reference substances, and specially prepared material, which are relatively fragile and differ markedly in stability and quality during storage, shall be retained only as long the quality of the preparation affords evaluation. Specimens obtained from mutagenicity tests, specimens of soil, water, and plants, and wet specimens of blood, urine, feces, biological fluids, do not need to be retained beyond quality assurance review. In no case shall retention be required for longer periods than those set forth in paragraph (b) of this section.

* * * * *

(i) Records required by this part may be retained either as original records or as true copies such as photocopies, microfilm, microfiche, or other accurate reproductions of the original records.

Subpart L—[Removed]

29. By removing Subpart L—*Environmental Testing Provisions*, consisting of §§ 792.225, 792.226, 792.228, and 792.232.

[FR Doc. 87-29512 Filed 12-24-87; 8:45 am]
BILLING CODE 6560-50-M

8.2.2 SUMMARY TOXICITY DATA ON DECONTAMINATED CHEMICAL AGENTS

Table 1. Summary Toxicity Data on Decontaminated Chemical Agents.

Test Samples	Toxicity Data[a]				
	Oral LD50 (Rat)	Reference	Dermal LD50 (Rabbit)	Reference	Inhalation LC50[c,d]
HD (5, 10, or 20% NaOH, pH 7)	> 50 mg/kg	Lab Notebook MN 2646 (103-104)	> 200 mg/kg	Lab Notebook MN 2646 (107)	> 2 mg/liter
HD #1 (CH_3OH/40% NaOH, pH 7)	> 50 mg/kg	Lab Notebook MN 2646 (74-75)	> 200 mg/kg	Lab Notebook MN 2646 (82)	> 2 mg/liter
HD #2 (triton X100, 20% NaOH, pH 7.0)	> 50 mg/kg	Lab Notebook MN 2646 (74-75)	> 200 mg/kg	Lab Notebook MN 2646 (83)	
HD #4 (methyl cellusolve, 20% NaOH)	>50 mg/kg	Lab Notebook MN 2646 (74-75)	> 200 mg/kg	Lab Notebook MN 2646 (83)	
HD ($CHCl_3$/5-20% NaOH, pH 7)	> 50 mg/kg	Lab Notebook MN 2647 (24)	> 200 mg/kg	Lab Notebook MN 2647 (27-28)	
HD (5, 10, or 20% NaOH)	> 50 mg/kg	Lab Notebook MN 2646 (103-104)	> 200 mg/kg	Lab Notebook MN 2646 (107)	
Lewisite (5, 10, or 20% NaOH, pH 7)	> 50 mg/kg	Lab Notebook MN 2646 (103)	> 200 mg/kg	Lab Notebook MN 2646 (108)	> 2 mg/liter
Lewisite ($CHCl_3$/NaOH)	> 50 mg/kg	Lab Notebook MN 2647 (32)	> 200 mg/kg	Lab Notebook MN 2647 (33)	> 2 mg/liter
5% HD/5% Lewisite ($CHCl_3$/NaOH (5, 10, 20%), pH 7)	> 50 mg/kg	Lab Notebook MN 2647 (22)	> 200 mg/kg	Lab Notebook MN 2647 (26-27)	

Table 1. Summary Toxicity Data on Decontaminated Chemical Agents (Continued).

Test Samples	Toxicity Data[a] Oral LD50 (Rat)	Reference	Dermal LD50 (Rabbit)	Reference	Inhalation LC50[c,d]
GB (H_2SO_4, pH 4)	> 50 mg/kg	Lab Notebook MN 2702 (78)	> 200 mg/kg	Lab Notebook MN 2702 (78)	
GB (detoxed, dried salts)	> 50 mg/kg	Lab Notebook MN 2702 (56)	> 200 mg/kg	Lab Notebook MN 2702 (57)	
GB (neutralized - Brine - dried salts)	889 mg/kg (24 hr)[b]	Lab Notebook MN 2646 (14-15)			
	568 mg/kg (14 day)[b]	Lab Notebook MN 2646 (14-15)			
GB (demil 09539)	566 mg/kg (24 hr)[b]	Lab Notebook MN 2646 (68-69)	> 200 mg/kg	Lab Notebook MN 2646 (82)	
	271 mg/kg (14 day)[b]	Lab Notebook MN 2646 (68-69)	> 2 g/kg[b]	Lab Notebook MN 2646 (91)	
GA (detoxified)	< 50 mg/kg	Lab Notebook MN 2702 (66)	> 200 mg/kg	Lab Notebook MN 2702 (66)	
VX (H_2O, pH 4.8)	> 50 mg/kg	Lab Notebook MN 2702 (79)	> 200 mg/kg	Lab Notebook MN 2702 (79)	
VX (detoxed, neutralized dried salts)	> 50 mg/kg	Lab Notebook MN 2702 (56)	> 200 mg/kg	Lab Notebook MN 2702 (57)	
VX (HTH)	> 50 mg/kg	Lab Notebook MN 2702 (118)	> 200 mg/kg	Lab Notebook MN 2702 (119)	

[a] Toxicity tests (oral, dermal, inhalation) per DOT guidelines unless otherwise stated.

[b] Toxicity tests (oral, dermal) per FDA guidelines.

[c] DOT inhalation tests, exposure time = 1 hour.

[d] Owens Memo (SAREA-BL-TE, 9 Sep 74).

BLANK PAGE

8.2.3 TYPE PROTOCOL 210880360000

TYPE PROTOCOL 210880360000

TITLE: Hazard Evaluation of Decontaminated Liquid Waste at CRDEC

DIRECTORATE/DIVISION: Chemical Research, Development and Engineering Center, Research Directorate, Toxicology Division, Biosciences Branch, Aberdeen Proving Ground, MD 21010-5423

RESPONSIBLE INVESTIGATOR(S):

Principal Investigator: James H. Manthei — 21/12/87 Date

Co-Investigators: John T. James, Ph.D. — 21/12/87 Date

Dale H. Heitkamp — 21/12/87 Date

Quality Assurance Dir: Dennis W. Johnson — 21/12/87 Date

Branch Chief: John T. James, Ph.D. — 21/12/87 Date
Acting Chief, Biosciences Branch

Division Chief: Harry Salem, Ph.D. — 22/12/87 Date
Chief, Toxicology Division

Director, Research: F. Prescott Ward — 22 DEC 87 Date
Dr. F. Prescott Ward, D.V.M., Ph.D.
Acting Director, Research

MANAGEMENT DATA:

Sponsor: Janis Chase — 24/12/87 Date
Chief, Environmental Quality Office

Protocol Number: 210880360000
Project Number:
Job Order Number:

1. Background.

In January 1986 the State of Maryland passed a regulation listing residues of certain decontaminated chemical surety material (CSM) as hazardous waste. Chemical Research, Development and Engineering Center (CRDEC) then initiated a delisting request for these residues, in that they do not meet the criteria for hazardous waste. CRDEC has tasked Research Directorate to provide both analytical and toxicological data that will support this delisting process.

Chemical Division will be designated to provide final decontaminated and neutralized products to Toxicology Division for a toxic hazard evaluation.

Since there exists several accepted decon procedures for many of the CSMs in question, it may become necessary to test one or more of these decon procedures with each of the CSMs.

To answer the questions posed to CRDEC by the State of Maryland in their 3 September 1987 letter, the following criteria must be met:

a. CRDEC must provide a detailed description of the actual decontamination procedures used on the laboratory materials. This must include a step-by-step outline of the decontamination process, and must identify the decontaminating agent used on a given CSM, the theoretical chemical reaction, the concentration of the decontaminating agent used, the amount of time the reaction is allowed to proceed, and any parameters that influence the degree to which the reaction goes to completion.

b. CRDEC must describe the procedures used to assure that the solutions on which toxicological tests are performed are equivalent to the solutions resulting from the actual decontamination procedures.

c. Finally, CRDEC must describe the protocol for the toxicological testing so that the State of Maryland can determine whether it follows generally accepted practices.

In line with the above questions, this Type protocol describes in detail the tests used by Toxicology Division to verify the decontamination of the CSM in question (Question c above). Toxicology Division will determine by the oral and inhalation route in rats, and by the dermal route in rabbits, that the CSM have been decontaminated to a level less than a Class "B" poison using currently approved test procedures as spelled out in CFR 49[1] (DOT tests). This protocol will be used as a Type protocol so any additional CSM or decon procedures can be evaluated by the same procedures as herein described.

The albino rat and New Zealand White (NZW) albino rabbit are the species of choice for "DOT" testing.

The rat and rabbit are the species of choice for these tests as specified in CFR 49.[1]

2. Hypothesis.

Chemical decontamination of CSM, followed by neutralization and subsequent oral, dermal and inhalation toxicity tests, will show that the original CSM have been decontaminated/deactivated to a toxicity level less than a class "B" poison and are no longer a hazardous substance and can be delisted from the State of Maryland's list of hazardous wastes..

3. Materials.

Test materials will be the decontaminated solutions of agents following their neutralization to pH of 7.0. The initial agents will be as chemically pure as available and they will then be decontaminated with an appropriate

caustic or acid as required, followed by a neutralization procedure. These procedures will be carried out by the Chemical group at CRDEC, and the finalized test samples will be provided to the Toxicology Division for testing. Details of the decontamination procedure, as well as the initial agent chemical purity and the neutralization procedure, along with the final pH, will become part of the final document.

4. Methods.

4.1 Procedure for Rat Oral Toxicity Screen.

A group of 10 young adult Sprague Dawley rats (5 each sex) weighing 200 to 300 gm will be given a single oral dose (intubation into stomach) of 50 milligrams per kilogram of the neutralized test substance. Those substances that produce death in half or more than half of the test group would be considered class"B" poisons as specified in CFR 49.

Detailed test procedures for this oral test involve the procurement of healthy Albino rats at least 7 days prior to start of the test. Upon arrival, rats will be quarantined and housed in a suitable room in Bldg E3222 that is climatically controlled to 70°F ± 3° and a relative humidity of 30-70%. Rats will be maintained on approved certified rodent chow and have both food and water available ad libitum during the quarantine. They will be housed two rats per cage, separated by sex and have hardwood chip bedding available. Stainless steel, sequentially-numbered, ear tags will be used for positive identification.

The night before oral dosage each rat will be fasted, but allowed to have access to water. Food should be removed between 1530 hr and 1630 hr the day prior to testing. On the next morning just prior to dosing, access to water will also be restricted. At the time of dosing each rat will be weighed to the nearest gm and then intubated with 0.050 ml/kg of the test substance using a bulb-tipped 16 gauge stainless steel feeding needle. The needle is carefully inserted into the esophagus, and the substance is injected directly into the stomach. All food and water is then withheld for 6 hours so as not to interfere with the complete absorption of the test substance. Each rat is observed for onset of toxic signs, and any deaths or toxic signs will be recorded for onset time, severity and duration. Since this is a 48 hour test, death is the primary endpoint. Following dosage, animals will be housed individually to prevent animal-to-animal interaction. After 48 hours, each rat will be weighed; those that die will be weighed post-mortem. Final disposition of all survivors will be euthanization by CO_2 inhalation.

Identification of each animal will be maintained by cage card and numbered S.S. ear tag during the test.

4.2 Procedures for Rabbit Dermal Toxicity Screen.

As specified in CFR 49, class "B" poisons are those substances that produce death in half or more than half of a group of 10 young adult rabbits weighing 2.3 to 3.0 kg following continuous dermal contact with the bare skin for 24 hours or less. Specifically, our test procedures will include the use

of a group of 10 young adult New Zealand White rabbits (5 each sex) following a quarantine of 7 days. Rabbits will be housed in single unit approved stainless steel cages and have approved certified rabbit chow and water available ad libitum. Quarantine and housing will be in room 106, Bldg E3222, prior to testing and in room 107, Bldg E3222, following testing. Both these rooms will be maintained at 70°F ± 3° and a relative humidity of 30-70%.

The day prior to testing (18-24 hr), each rabbit will be clipped free of hair on the dorsum (back) (approximately 150 sq cm area) using two small animal electric clippers. One clipper will be fitted with a number 2 blade (first clipping) and the second clipping will be done with a number 40 blade. Clipped hair will be removed immediately by vacuum. Each rabbit is returned to its home cage following the clipping procedure.

The next morning, each rabbit, in groups of 10 (5 each sex) will be weighed to the nearest one-hundredth of a kilogram, its metal ear tag number recorded, and each animal will be tattooed with a black ink sequential number inside the left ear.

In order to apply the test material to the skin, each rabbit will be manually restrained by two individuals, and a 2" by 2", two-layer thick surgical gauze patch will be taped to the skin with hypoallergenic tape. At this time a dose of test substance is applied to the skin under the gauze at a volume of 0.200 ml/kg. The gauze is then immediately covered with polyethylene film which is, in turn, tape secured to the clipped skin with additional hypoallergenic tape to form a semi-occlusive protective covering. This procedure is followed by fitting an Elizabethan collar around each rabbit's neck to prevent the animal's licking or scratching at the test site. After the collar is secured, the rabbit is returned to its home cage and the patch is left intact for 24 hours. Rabbits will have free access to food and water and observation for toxic signs and death will continue for 48 hrs. The test patch is removed after 24 hrs, the skin is gently rinsed with lukewarm water, blotted dry, and the rabbit again returned to its home cage.

After the 48 hr test is completed, all surviving rabbits will be euthanized by intravenous (ear vein) injection with T-61 (0.20 ml/kg).

Toxic signs will be carefully observed and recorded both for onset time and severity, as well as duration. Since these decontaminated substances were prepared from either nerve agents or irritants/vesicants, any residual, non-decontaminated agent, should produce either visible toxic signs or skin irritation.

4.3 Procedures for Rat Inhalation Toxicity Screens.

CFR 49 states that a class "B" poison is a vapor, mist, or dust that when continuously inhaled at a concentration of 2 milligrams per liter or less for 1 hr produces death in half or more than half of a group of 10 white laboratory rats (200 to 300 gm) within 48 hours.

Of the 8 compounds listed in Table 1, only 5 have sufficient vapor pressure to be of concern as inhalation hazards. They will be tested under conditions designed to demonstrate any inhalation hazard. The inhalation

hazard test recognizes that both volatility and toxicity affect the hazard potential in the workplace. To address these two areas in the complex decon solution, the experimental protocol has been specified as outlined below:

a. Place 5 young adult rats of one sex (acclimated in the animal room for at least 5 days) in an inhalation chamber of $\leq$ 20 liters volume. For each test compound 10 rats are exposed in 2 groups of 5 each, with males and females exposed to each test material. The apparatus is diagrammed in Figure 1.

b. Draw exposure atmosphere through a 5 cm column of the test liquid.

c. Exposure time is 1 hour and the test liquid must be replenished 30 min into the exposure.

The goal is to show <5 deaths for 48 hr after the exposure. This would indicate less than a class B poison.

It should be noted that this procedure gives a maximal concentration compared to that expected in the laboratory. Attempting to directly generate 2 mg/l of the decon material would be technically difficult and would be irrelevant to the workplace hazard. In addition, no attempt will be made to quantitate chamber contents as this would be expected to be a highly complex mixture undergoing rapid change as the more volatile components of the test solution are exhausted. During exposure the chamber temperature will be maintained at 23 $\pm$ 2°C, and once during each exposure the O_2 content will be checked.

5. Technical Methods.

5.1 Rats.

Rats used for oral dosing will be housed in Bldg E3222, room to be determined (possibly 108), which is climatically controlled to 70°F $\pm$ 3° and a relative humidity of 30-70%. Daylight/dark hours will be controlled by timer on a 12-hour cycle. Rat cages will be standard size polycarbonate, containing hardwood chip bedding. During quarantine, rats will be housed in groups of two, by sex, and have certified rodent chow and water available ad libitum. Bedding will be changed on Mondays, Wednesdays and Fridays and food and water will be checked daily. After testing, rats will be housed individually to prevent animal-to-animal contact and cannibalism. Observation for toxic signs will be continuous on test day, and at least three times on day two, or more often if toxic signs persist. After 48 hours all surviving rats will be euthanized by CO_2 inhalation.

Rats used in the inhalation phase of this study will be housed in room 4 of building E3226. Environmental parameters are as above. Caging will be individually, however. Euthanization will be by CO_2 inhalation.

5.2 Rabbits.

Rabbits will be housed in room 106, building E3222, during quarantine. Each rabbit will be in a single unit stainless steel cage and have approved rabbit chow and water available ad libitum. Food and water are checked daily and cage pans are sanitized on Mondays, Wednesdays and Fridays. The temperature will be automatically controlled to within 70°F ± 3°, and relative humidity, 30-70%; light cycles will be maintained automatically with a 12 hour daylight/12 hour dark cycle. Body weights will be monitored upon arrival, at test time, and then at termination or death, whichever occurs first. Identification will be by sequentially-numbered metal ear tag, as well as an identical number tattooed in black ink on the inner surface of the left ear.

Test procedures will be done in rm 107, building E3222, and this room will be environmentally maintained the same as in room 106. Rabbits will be prepared for testing by clipping a 150 sq cm area on their dorsal area using both a number 2 and a number 40 blade attached to small animal clippers. Elizabethan collars will be worn by each rabbit for the duration of the 24 hr exposure to prevent licking and disturbing the test site. Following test completion, rabbits will be euthanized by intravenous injection (ear vein) of T-61 (0.20 ml/kg).

6. Data Analysis.

Data analysis will involve monitoring and recording the onset and duration of toxic signs, as well as times to death. Those substances producing death in half, or more than half, of each group of 10 animals will be considered as class "B" poisons. Since several of the test starting agents substances may produce irritation, this toxic effect will also be monitored.

7. Compound Purity.

The initial starting compounds that will be decontaminated/deactivated by combining them with either bases or acids will be as pure as available at CRDEC and the decontamination materials will be documented by the chemists and supplied for inclusion in the final document. Also to be included is the pH of the final neutralized product.

8. Data Storage.

Test data will be recorded in official CRDEC notebooks along with any computerized data developed. Ultimately, these will be reported in a technical report and final disposition of the test data will be in the Toxicology Division Archives.

The type of data to be recorded include:

a. Animal species, sex, weight, ear tag number.

b. Animal arrival date, test date, termination date.

c. Complete record of toxic signs observed, as well as time of deaths if they occur.

d. Record of feed used, lot number, brand, manufacturer.

e. Times for inhalation exposure.

f. Complete record of chemical substances used, to include starting purity of the agents, decontamination procedures, and the final neutralization procedure, as well as the final pH.

g. Names of individuals involved in the study, along with their qualifications.

h. Record of facility climatic conditions.

i. Any problems that arise, such as climatic, animal health status during quarantine will be documented.

j. Any changes necessary to the procedures spelled out in this protocol will be documented.

9. Pain Category.

Although these substances are to be detoxified and neutralized, the oral and dermal test procedures in themselves will produce some stress. The oral and dermal tests will therefore be conducted as pain/stress without anesthetic or analgesics. The inhalation tests will produce no significant pain or stress.

10. Euthanasia.

Following the completion of the 48 hour test procedure, rats will be euthanized by inhalation of CO_2 and rabbits will be terminated by intravenous (ear vein) injection of T-61 (euthanasia solution), at a volume of 0.2 ml/kg.

11. Bibliography.

1. Code of Federal Regulations, CFR 49 (Transportation) parts 100 to 177, Section 173.343 Poison B, page 602, October 1, 1986.

12. Coordination.

a. Clinical Pathology: None required

b. Anatomical Pathology: None required

c. Animal Requirements:

(1) Species: Rabbit

Strain: NZW

Total Number: 10 per test

Age and Weight: Young adult, 2.3 to 3.0 kg

Sex: 5 male and 5 female per test

Starting Date: Open

Completion Date: Open

(2) Species: Rat

Strain: Sprague-Dawley

Total Number: 20 per test

Age and Weight: Young adult, 200 to 300 gm

Sex: 10 male and 10 female per test

Starting Date: Open

Completion Date: Open

d. Cost Accounting:

(1) Protocol Number:

(2) Project Number:

(3) Job Order Number:

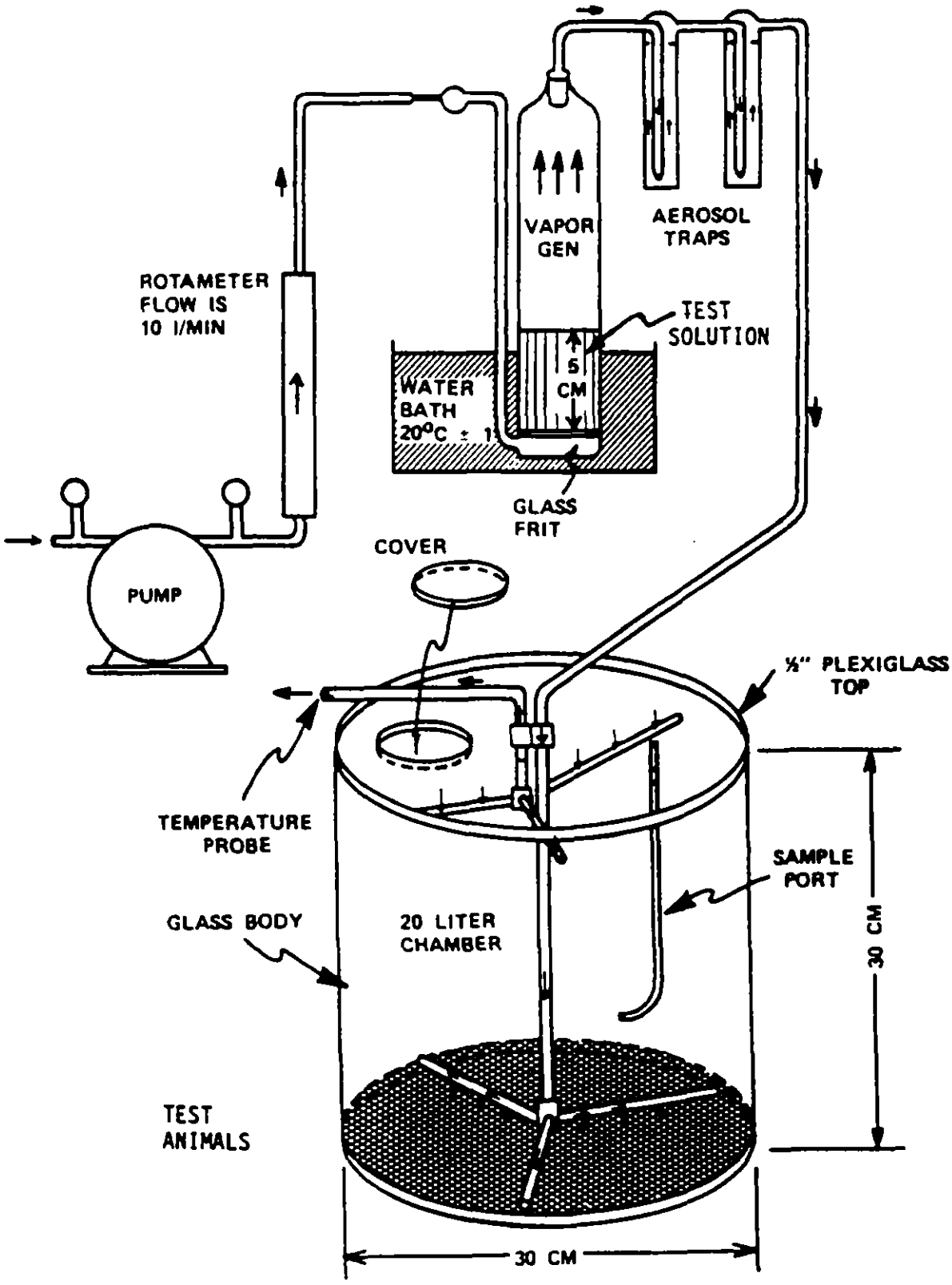


Figure 1. Inhalation Hazard Test of Deconned Agent Solution

8.2.4 CODE OF FEDERAL REGULATIONS DEPARTMENT OF TRANSPORTATION GUIDELINES FOR CLASSES OF POISONOUS MATERIALS

code of federal regulations

49

Transportation

PARTS 100 TO 199

Revised as of December 31, 1976

... discharge openings are not permitted.

[Order 66, 30 FR 5745, Apr. 23, 1965, as amended by Order 71, 31 FR 9070, July 1, 1966. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-60, 37 FR 2686, Feb. 3, 1972, 37 FR 3524, Feb. 17, 1972; Amdt. 173-94, 41 FR 16074, Apr. 15, 1976]

Subpart F—Corrosive Materials: Definition and Preparation

Source: 29 FR 18725, Dec. 29, 1964, unless otherwise noted. Redesignated at 32 FR 5606, Apr. 5, 1967.

§ 173.240 Corrosive material; definition.

(a) For the purpose of this subchapter, a corrosive material is a liquid or solid that causes visible destruction or irreversible alterations in human skin tissue at the site of contact, or in the case of leakage from its packaging, a liquid that has a severe corrosion rate on steel.

(1) A material is considered to be destructive or to cause irreversible alteration in human skin tissue if when tested on the intact skin of the albino rabbit by the technique described in Appendix A to this Part, the structure of the tissue at the site of contact is destroyed or changed irreversibly after an exposure period of 4 hours or less.

(2) A liquid is considered to have a severe corrosion rate if its corrosion rate exceeds 0.250 inch per year (IPY) on steel (SAE 1020) at a test temperature of 130° F. An acceptable test is described in NACE Standard TM-01-69.

(b) If human experience or other data indicate that the hazard of a material is greater or less than indicated by the results of the tests specified in paragraph (a) of this section, the Department may revise its classification or make the material subject to the requirements of Parts 170–189 of this subchapter.

[Amdt. 173-61, 37 FR 5947, Mar. 23, 1972; as amended by Amdt. 173-76, 38 FR 20839, Aug. 3, 1973; Amdt. 173-94, 41 FR 16074, Apr. 15, 1976]

§ 173.241 Outage.

(a) The outage (ullage) for packagings containing corrosive liquids, when offered for transportation, must be in accordance with the following requirements:

(1) *General outage requirements.* Packagings must not be completely filled. The proper vacant space (outage) in a tank car or other shipping container depends on the coefficient of expansion of the liquid and the maximum increase of temperature to which it will be subjected in transit. Outage must be calculated to the total capacity of the container.

(2) *Outage requirements for packagings of 110 gallons or less.* Sufficient outage must be provided so that the packaging will not be liquid full at 130° F. (55° C.).

(3) *Outage requirements for tank cars.* In tank cars, outage must be calculated to percentage of the total capacity of the tank, i. e., shell and dome capacity combined. If the dome of the tank car does not provide sufficient outage, then vacant space must be left in the shell to make up the required outage. The outage for tank cars must be not less than 1 percent.

(4) *Outage requirements for cargo tanks or portable tanks.* No cargo tank or portable tank, or compartment thereof, used for the transportation of any corrosive liquid shall be completely filled. The outage for cargo tanks and portable tanks must be no less than 2 percent.

[29 FR 18725, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-61, 37 FR 5947, Mar. 23, 1972; Amdt. 173-94, 41 FR 16074, Apr. 15, 1976]

§ 173.242 Bottles containing corrosive liquids.

(a) Bottles containing corrosive liquids, as defined by § 173.240, may not be packed in the same outside container with any other article, except as specifically provided in paragraphs (b) and (c) of this section and §§ 173.25, 173.257, 173.258, 173.259, 173.260, 173.261, or 173.288.

(b) Bottles containing corrosive liquids cushioned by incombustible absorbent material and securely packed in tightly closed metal containers, except hydrofluoric acid which must be packed in a container other than a metal container, may be packed with other articles. This exception does not apply to nitric acid exceeding 40 percent concentration, perchloric acid, hydrogen peroxide exceeding 52 percent strength by weight, nitrohydrochloric acid, or nitrohydrochloric acid diluted, which must not be packed in the same outside container with any other article under any circumstances.

[1] Amdt. 173-61, 37 FR 5947, Mar. 23, 1972.

vate and contract motor carriers under conditions specified in § 177.840(a)(1) of this subchapter.

(vii) Pressure in each cylinder must be reduced to 8 psig or lower at least once within 4 hours before the beginning of transportation.

[29 FR 18743, Dec. 29, 1964. Redesignated at 32 FR 5606, and amended by Amdt. 173-6, 34 FR 7161, May 1, 1969, Amdt. 173-94, 41 FR 16081, Apr. 15, 1976]

Subpart H—Poisonous Materials, Etiologic Agents, and Radioactive Materials; Definitions and Preparation

Source: 29 FR 18753, Dec. 29, 1964, unless otherwise noted. Redesignated at 32 FR 5606, Apr. 5, 1967.

§ 173.325 Classes of poisonous materials.

(a) Poisonous materials for the purpose of this subchapter are divided into three groups according to the degree of hazard in transportation.

(1) Poison A.

(2) Poison B.

(3) Irritating material.

[Amdt. 173-94, 41 FR 16081, Apr. 15, 1976]

§ 173.326 Poison A.

(a) For the purpose of Parts 170–189 of this subchapter extremely dangerous poisons, class A, are poisonous gases or liquids of such nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life. This class includes the following:

(1) Bromacetone

(2) Cyanogen.

(3) Cyanogen chloride containing less than 0.9 percent water.

(4) Diphosgene.

(5) Ethyldichlorarsine.

(6) Hydrocyanic acid (see Note 1 of this paragraph).

(7) [Reserved]

(8) Methyldichlorarsine.

(9) [Reserved]

(10) Nitrogen peroxide (tetroxide).

(11) [Reserved]

(12) Phosgene (diphosgene).

(13) Nitrogen tetroxide-nitric oxide mixtures containing up to 33.2 percent weight nitric oxide.

Note 1: Diluted solutions of hydrocyanic acid of not exceeding 5 percent strength are classed as poisonous articles, class B (see § 173.345).

(b) Poisonous gases or liquids, class A, as defined in paragraph (a) of this section, except as provided in § 173.331, rail express.

[29 FR 18753, Dec. 29, 1964. Redesignated 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-94, 41 FR 16081, Apr. 15, 1976; Amdt. 173-94A, 41 FR 40683, Sept. [illegible]

§ 173.327 General packaging requirements for Poison A materials.

(a) Cylinders must be maintained in compliance with the requirements of § 173.34. Valves must be capable of withstanding the test pressure of the cylinders and must have taper-threaded connections directly to the cylinders. Bushings or straight-threaded connections of valves to cylinders permitted. For corrosive commodities, valves may be of the packed type provided the assembly is made gas-tight by means of a seal cap with compatible gasketed joint to the valve body or to the cylinder to prevent loss of commodity through or past the packing; otherwise the valves must be of the packless type with nonperforated diaphragms and handwheels. Each valve outlet must be sealed by a threaded cap or a threaded solid plug. The outlet caps and plugs, luting, and gaskets must be compatible with each other, the valve assembly, and the lading.

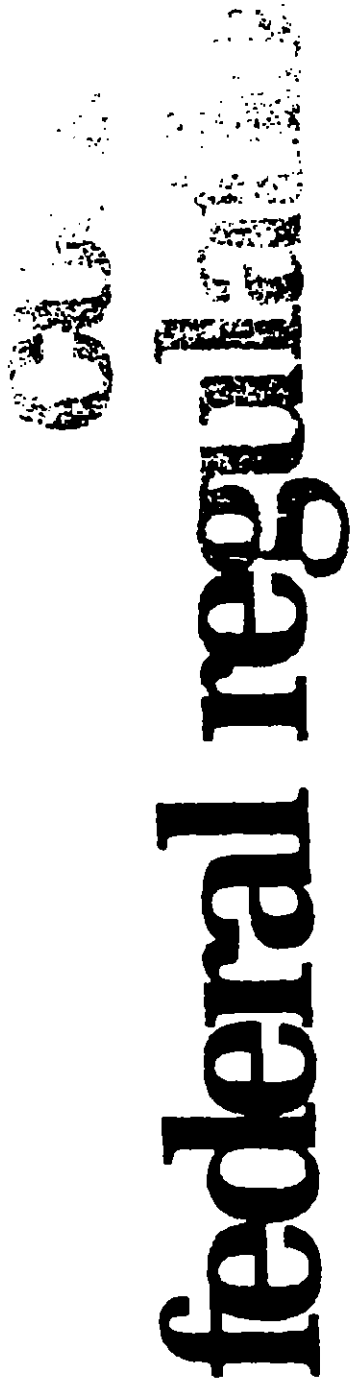
(1) The pressure of the poison gas at 130° F. must not exceed the service pressure of the cylinder. Cylinders must not be liquid full at 130° F.

(2) Cylinders packed in boxes must have adequate protection for valves. Box and valve protection must be of strength sufficient to protect all parts of cylinders and valves from deformation or breakage resulting from a drop of at least 6 feet onto a concrete floor, impacting at the weakest point. A cylinder not overpacked in a box must be equipped with a protective cap or other means of valve protection which must be capable of preventing damage to or distortion of the valve if it were subjected to an impact test as follows: The cylinder, prepared as for shipment, is allowed to fall from an upright position with the side of the cap or other valve protection striking a solid steel object projecting not more than 6 inches above the floor level.

(b) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(c) No class A poisons in cargo tanks. No "extremely dangerous poison, class

Transportation



49

PARTS 100 TO 177

Revised as of October 1, 1986

CONTAINING
A CODIFICATION OF DOCUMENTS
OF GENERAL APPLICABILITY
AND FUTURE EFFECT

AS OF October 1, 1986

With Ancillaries

Published by
the Office of the Federal Register
National Archives and Records
Administration

as a Special Edition of
the Federal Register

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967 and amended by Amdt. 173-73, 38 FR 20085, July 27, 1973; Amdt. 173-94, 41 FR 16083, Apr. 15, 1976]

§ 173.338 [Reserved]

§ 173.343 Poison B.

(a) For the purposes of Parts 170-189 of this subchapter and except as otherwise provided in this Part, class B poisons are those substances, liquid or solid (including pastes and semisolids), other than Class A poisons or Irritating materials, which are known to be so toxic to man as to afford a hazard to health during transportation; or which, in the absence of adequate data on human toxicity, are presumed to be toxic to man because they fall within any one of the following categories when tested on laboratory animals:

(1) *Oral toxicity.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams at a single dose of 50 milligrams or less per kilogram of body weight, when administered orally.

(2) *Toxicity on inhalation.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams, when inhaled continuously for a period of one hour or less at a concentration of 2 milligrams or less per liter of vapor, mist, or dust, provided such concentration is likely to be encountered by man when the chemical product is used in any reasonable foreseeable manner.

(3) *Toxicity by skin absorption.* Those which produce death within 48 hours in half or more than half of a group of 10 or more rabbits tested at a dosage of 200 milligrams or less per kilogram body weight, when administered by continuous contact with the bare skin for 24 hours or less.

(b) The foregoing categories shall not apply if the physical characteristics or the probable hazards to humans as shown by experience indicate that the substances will not cause serious sickness or death. Neither the display of danger or warning labels pertaining to use nor the toxicity tests set forth above shall prejudice or prohibit the exemption of

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-94, 41 FR 16083, Apr. 15, 1976; Amdt. 173-94B, 41 FR 57070, Dec. 30, 1976]

§ 173.344 General packaging requirements for Poison B liquids.

(a) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(b) Packagings containing liquid material may not be completely filled. Outage must be as follows:

(1) For packagings of 110 gallons or less, sufficient outage must be provided so that the packaging will not be liquid full at 130° F. (55° C.).

(2) The proper vacant space (outage) in a tank car or other shipping container depends on the coefficient of expansion of the liquid and the maximum increase of temperature to which it will be subjected in transit. Outage must be calculated to the total capacity of the container.

(3) Liquid poison must not be loaded into domes of tank cars.

(4) In tank cars, outage must be calculated to percentage of the total capacity of the tank, i. e., shell and dome capacity combined. If the dome of the tank car does not provide sufficient outage, then vacant space must be left in the shell to make up the required outage.

(5) The outage for tank cars must not be less than 1 percent.

(6) No cargo tank or compartment thereof used for the transportation of any liquid poison shall be completely filled; sufficient space shall be left vacant in every case to prevent leakage from or distortion of any such cargo tank by expansion of the contents due to rise in temperature in transit, and such free space (outage) shall be sufficient in every case so that such cargo tank shall not become entirely filled with the liquid at 130° F.

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-94, 41 FR 16083, Apr. 15, 1976. Amdt. 173-94A, 41 FR 40683, Sept. 20, 1976]

§ 173.345 Limited quantities of Poison B liquids.

(a) Limited quantities of Poison B liquids for which exceptions are per-

Transportation

federal regulations

49

PARTS 100 TO 177

Revised as of October 1, 1986

CONTAINING
A CODIFICATION OF DOCUMENTS
OF GENERAL APPLICABILITY
AND FUTURE EFFECT

AS OF October 1, 1986

With Ancillaries

Published by
the Office of the Federal Register
National Archives and Records
Administration

as a Special Edition of
the Federal Register

with inert luting or gasket material. Valves must be of stainless steel and the caps, plugs, and valve seats must be of material that will not be deteriorated by contact with nitric oxide or nitrogen dioxide. The tank may not be equipped with any safety relief device.

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-73, 38 FR 20085, July 27, 1973; Amdt. 173-94, 41 FR 16082, Apr. 15, 1976; Amdt. 173-52, 46 FR 62458, Dec. 24, 1981; 47 FR 13818, Apr 1, 1982]

§ 173.343 Poison B.

(a) For the purposes of Parts 170-189 of this subchapter and except as otherwise provided in this part, Class B poisons are those substances, liquid or solid (including pastes and semisolids), other than Class A poisons or Irritating materials, which are known to be so toxic to man as to afford a hazard to health during transportation; or which, in the absence of adequate data on human toxicity, are presumed to be toxic to man because they fall within any one of the following categories when tested on laboratory animals:

(1) *Oral toxicity.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams at a single dose of 50 milligrams or less per kilogram of body weight, when administered orally.

(2) *Toxicity on inhalation.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams, when inhaled continuously for a period of one hour or less at a concentration of 2 milligrams or less per liter of vapor, mist, or dust, provided such concentration is likely to be encountered by man when the chemical product is used in any reasonable foreseeable manner.

(3) *Toxicity by skin absorption.* Those which produce death within 48 hours in half or more than half of a group of 10 or more rabbits tested at a dosage of 200 milligrams or less per kilogram body weight, when administered by continuous contact with the bare skin for 24 hours or less.

(b) The foregoing categories shall not apply if the physical characteristics or the probable hazards to humans as shown by experience indicate that the substances will not cause serious sickness or death. Neither the display of danger or warning labels pertaining to use nor the toxicity tests set forth above shall prejudice or prohibit the exemption of any substances from the provisions of Parts 170-189 of this chapter.

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-94, 41 FR 16083, Apr. 15, 1976; Amdt. 173-94B, 41 FR 57070, Dec. 30, 1976]

§ 173.344 General packaging requirements for Poison B liquids.

(a) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(b) Packagings containing liquid material may not be completely filled. Outage must be as follows:

(1) For packagings of 110 gallons or less, sufficient outage must be provided so that the packaging will not be liquid full at 130° F. (55° C.).

(2) The proper vacant space (outage) in a tank car or other shipping container depends on the coefficient of expansion of the liquid and the maximum increase of temperature to which it will be subjected in transit. Outage must be calculated to the total capacity of the container.

(3) Liquid poison must not be loaded into domes of tank cars.

(4) In tank cars, outage must be calculated to percentage of the total capacity of the tank, i. e., shell and dome capacity combined. If the dome of the tank car does not provide sufficient outage, then vacant space must be left in the shell to make up the required outage.

(5) The outage for tank cars must not be less than 1 percent.

(6) No cargo tank or compartment thereof used for the transportation of any liquid poison shall be completely filled; sufficient space shall be left vacant in every case to prevent leakage from or distortion of any such

with inert luting or gasket material. Valves must be of stainless steel and the caps, plugs, and valve seats must be of material that will not be deteriorated by contact with nitric oxide or nitrogen dioxide. The tank may not be equipped with any safety relief device.

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-73, 38 FR 20085, July 27, 1973; Amdt. 173-94, 41 FR 16082, Apr. 15, 1976; Amdt. 173-52, 46 FR 62458, Dec. 24, 1981; 47 FR 13818, Apr 1, 1982]

§ 173.343 Poison B.

(a) For the purposes of Parts 170-189 of this subchapter and except as otherwise provided in this part, Class B poisons are those substances, liquid or solid (including pastes and semisolids), other than Class A poisons or Irritating materials, which are known to be so toxic to man as to afford a hazard to health during transportation; or which, in the absence of adequate data on human toxicity, are presumed to be toxic to man because they fall within any one of the following categories when tested on laboratory animals:

(1) *Oral toxicity.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams at a single dose of 50 milligrams or less per kilogram of body weight, when administered orally.

(2) *Toxicity on inhalation.* Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams, when inhaled continuously for a period of one hour or less at a concentration of 2 milligrams or less per liter of vapor, mist, or dust, provided such concentration is likely to be encountered by man when the chemical product is used in any reasonable foreseeable manner.

(3) *Toxicity by skin absorption.* Those which produce death within 48 hours in half or more than half of a group of 10 or more rabbits tested at a dosage of 200 milligrams or less per kilogram body weight, when administered by continuous contact with the bare skin for 24 hours or less.

(b) The foregoing categories shall not apply if the physical characteristics or the probable hazards to humans as shown by experience indicate that the substances will not cause serious sickness or death. Neither the display of danger or warning labels pertaining to use nor the toxicity tests set forth above shall prejudice or prohibit the exemption of any substances from the provisions of Parts 170-189 of this chapter.

[29 FR 18753, Dec. 29, 1964. Redesignated at 32 FR 5606, Apr. 5, 1967, and amended by Amdt. 173-94, 41 FR 16083, Apr. 15, 1976; Amdt. 173-94B, 41 FR 57070, Dec. 30, 1976]

§ 173.344 General packaging requirements for Poison B liquids.

(a) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(b) Packagings containing liquid material may not be completely filled. Outage must be as follows:

(1) For packagings of 110 gallons or less, sufficient outage must be provided so that the packaging will not be liquid full at 130° F. (55° C.).

(2) The proper vacant space (outage) in a tank car or other shipping container depends on the coefficient of expansion of the liquid and the maximum increase of temperature to which it will be subjected in transit. Outage must be calculated to the total capacity of the container.

(3) Liquid poison must not be loaded into domes of tank cars.

(4) In tank cars, outage must be calculated to percentage of the total capacity of the tank, i. e., shell and dome capacity combined. If the dome of the tank car does not provide sufficient outage, then vacant space must be left in the shell to make up the required outage.

(5) The outage for tank cars must not be less than 1 percent.

(6) No cargo tank or compartment thereof used for the transportation of any liquid poison shall be completely filled; sufficient space shall be left vacant in every case to prevent leakage from or distortion of any such

federal register

THURSDAY, JANUARY 24, 1974
WASHINGTON, D.C.

Volume 39 ■ Number 17

PART II

DEPARTMENT OF TRANSPORTATION

Hazardous Materials Regulations Board

■

CONSOLIDATION OF HAZARDOUS MATERIALS REGULATIONS AND MISCELLANEOUS PROPOSALS

Notice of Proposed Rulemaking

No. 17—Pt. II——1

H. Section 173.308 would be added to read as follows:

§ 173.308 Cigarette lighter or other similar device charged with fuel.

(a) In addition to the requirements of § 173.21(d), a cigarette lighter or other similar device charged with butane, a butane mixture, or other gaseous mixture having similar properties must be shipped in accordance with the following:

(1) No more than 2.3 fluid ounces of liquefied gas may be loaded into each device;

(2) The pressure in each device may not exceed 140 p.s.i.g. at 130°F.

(3) The liquid portion of the gas may not exceed 85 percent of the volumetric capacity of each fluid chamber at 60°F.

(4) Each device, including closures, must be capable of withstanding an internal pressure of at least 275 p.s.i.g.

(5) Devices must be overpacked in packaging that is designed or arranged to prevent movement of the device itself.

I. In § 173.314, the word chapter would be amended to read "subchapter" in paragraph (b)(4); paragraphs (b)(5) and (6) would be added to read as follows:

§ 173.314 Requirements for compressed gases in tank cars.

* * * * *

(b) * * *

(5) Each tank car, except series 106A*** or 110A*** containing a flammable compressed gas or flammable compressed gas mixture must be marked with the name of contents (§ 172.101) in accordance with the requirements of § 173.310 of this subchapter or as otherwise approved by the Department.

(6) Each tank car containing anhydrous ammonia or chlorine must be marked "ANHYDROUS AMMONIA" or "CHLORINE," as appropriate, in accordance with the requirements of § 173.310 of this subchapter.

§§ 173.315 and 173.316 [Amended]

J. Sections 173.315 and 173.316 would remain the same as now written except the word chapter would be amended to read "subchapter" each time it appears in the sections.

K. Subpart G would be amended as follows:

Subpart G—Extremely and Highly Toxic Materials; Etiologic Agents, and Radioactive Materials, Definitions ad Preparation

A. Section 173.325 would be amended to read as follows:

§ 173.325 Classes of poisonous materials.

(a) Poisonous materials for the purpose of this subchapter are divided into three groups according to the degree of hazard in transportation.

(1) Extremely toxic materials;

(2) Highly toxic material;

(3) Irritating material.

B. Section 173.326 would be deleted and a new § 173.326 would be added to read as follows:

§ 173.326 Extremely toxic materials; definition.

(a) For the purpose of this subchapter, a substance is considered to be an extremely toxic material if it falls within any one of the following categories when tested on laboratory animals according to the test procedures described in this paragraph:

(1) *Ingestion (oral).* Any material that has a single dose LD_{50}[1] of 5 milligrams or less per kilogram of body weight when administered orally to both male and female white rats (young adults);

(2) *Inhalation.* Any material that has an LC_{50}[1] of 50 parts per million or less by volume of a gas or vapor, or 0.50 milligram or less of mist or dust per liter of air when administered by continuous inhalation for 1 hour to both male and female white rats (young adults). If the material is administered to the animals as a dust or mist, more than 90 percent of the particles available for inhalation in the test must have a diameter of 10 microns or less, provided it is reasonably foreseeable that such concentrations could be encountered by man in transportation;

(3) *Skin absorption.* Any material that has an LD_{50} of 20 milligrams or less per kilogram of body weight when administered by continuous contact for 24 hours with the bare skin of rabbits according to the test procedures described in Appendix I to this part.

(b) If human experience or other data indicate that the hazard of a given material encountered during an accidental exposure in transportation is greater or less than indicated by the data from the specified animal tests, the Board may revise the classification for the specific material.

C. Section 173.326a would be added to read as follows:

§ 173.326a Highly toxic materials; definition.

(a) For the purpose of this subchapter, a substance is considered to be a highly toxic material if it falls within any one of the following categories when tested on laboratory animals according to the test procedures described in this paragraph:

(1) *Ingestion (oral).* Any material that has a single dose LD_{50}[1] of more than 5 milligrams but not more than 50 milligrams per kilogram of body weight when orally administered to both male and female white rats (young adults);

(2) *Inhalation.* Any material that has an LC_{50}[1] of more than 50 parts per million by volume of gas or vapor but not more than 500 parts per million or more than 0.50 milligram, but not more than 2 milligrams of mist or dust per liter of air when administered by continuous inhalation for 1 hour or less to both male and female white rats (young adults). If the product is administered to the animals as a dust or mist, more than 90 percent of the particles available for inhalation in the test must have a diameter of 10 microns or less provided it is reasonably foreseeable that such concentrations could be encountered by man in transportation.

(3) *Skin absorption.* Any material that has an LD_{50} of greater than 20 milligrams but not more than 200 milligrams per kilogram of body weight when administered by continuous contact for 24 hours with the bare skin of rabbits, according to the test procedures described in Appendix I to this Part.

(b) If human experience or other data indicate that the hazard of a given material encountered during an accidental exposure in transportation is greater or less than indicated by the data from the specified animal tests, the Board may revise the classification for the specific material.

D. Section 173.326b would be added to read as follows:

§ 173.326b Irritating materials; definition.

For the purpose of this subchapter, a substance is considered to be an irritating material if it causes reversible local irritant effects on eyes, nose, or throat temporarily impairing a person's ability to function to the degree that he cannot take necessary emergency action in the event of leakage.

E. In § 173.327, the heading and paragraphs (c) and (d) would be amended; paragraph (e) would be added to read as follows:

§ 173.327 General packaging requirements for extremely toxic materials.

* * * * *

(c) The transportation of an extremely toxic material is not permitted if there is any type of interconnection between packagings.

(d) No packaging used for the transportation of any liquid material may be completely filled. Sufficient space must be left empty of liquid to prevent leakage from distortion of the packaging caused by expansion of the contents due to rise in temperature during transportation. This free space must be sufficient in each packaging so that it will not become entirely filled with liquid at 130°F.

(e) Each tank car except series 106A*** and 110A***, must be marked with the name of contents (§ 172.101) in accordance with the requirements of § 173.310 of this subchapter.

F. Section 173.328 would be deleted and a new § 173.328 would be added to read as follows:

§ 173.328 Extremely toxic materials not specifically provided for.

(a) Extremely toxic materials, as defined in § 173.326, other than those for which special packaging requirements are prescribed in this part, must be packaged as follows:

(1) Specification 2S* or 3D of Part 178 of this subchapter). Metal containers of not over 126 pounds water capacity (nominal). Closures, if used, must be [illegible]

[1] LD_{50}, LC_{50}: That dose (LD) or concentration (LC) which will cause death within 14 days to one half of the test animals.

* Use of existing cylinders authorized, but new construction not authorized.

Background Document I, Reference 9

Edgewood Arsenal, 1974, Chemical Agent Data Sheets, Special Report EO-SR-74001, Vol. 1, Headquarters, Edgewood Arsenal, Aberdeen Proving Ground, Md. (Dec.).

See Background Document B, Reference 15

Background Document I, reference 10

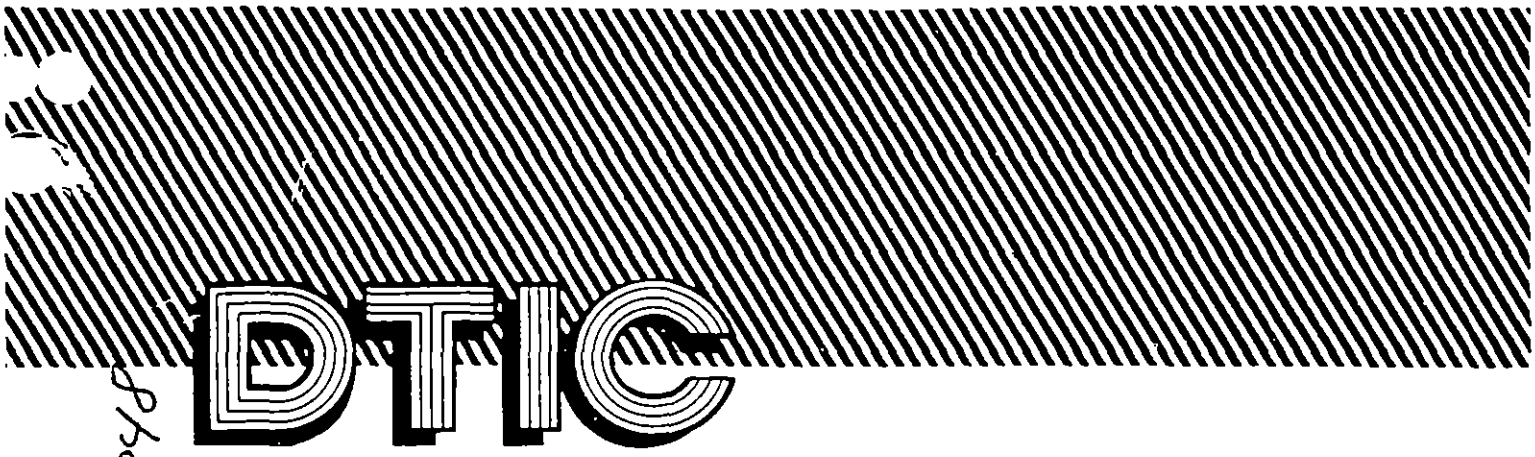
Hewett, C.L., 1948, "Isomers of 2-Chlorovinyldichloroarsine," J. Chem. Soc. 1203-1205.

See Background Document B, Reference 26

Background Document I, reference 11

Jackson, K.E., and M.A. Jackson, 1935, "The Chlorovinylarsines," Chem. 16:429-452.

See Background Document B, Reference 29



Technical Report

distributed by

Defense Technical Information Center
DEFENSE LOGISTICS AGENCY
Cameron Station • Alexandria, Virginia 22314

NOTICE

We are pleased to supply this document in response to your request.

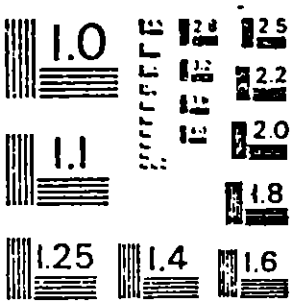
The acquisition of technical reports, notes, memorandums, etc., is an active, ongoing program at the Defense Technical Information Center (DTIC) that depends, in part, on the efforts and interests of users and contributors.

Therefore, if you know of the existence of any significant reports, etc., that are not in the DTIC collection, we would appreciate receiving copies or information related to their sources and availability.

The appropriate regulations are Department of Defense Directive 5100.36, Defense Scientific and Technical Information Program; Department of Defense Directive 5200.20, Distribution Statements on Technical Documents; Military Standard (MIL-STD) 847-A, Format Requirements for Scientific and Technical Reports Prepared by or for the Department of Defense; Department of Defense Regulation 5200.1-R, Information Security Program Regulation.

Our Acquisition Section, DTIC-DDA-1, will assist in resolving any questions you may have. Telephone numbers of that office are: (202) 274-6847, 274-6874 or Autovon 284-6847, 284-6874

June 1982



MICROCOPY RESOLUTION TEST CHART

Report DRXTH-TE-CR-83209

(11)

DEVELOPMENT OF CHEMICAL PROCESSES FOR CHEMICAL DEMILITARIZATION--PHASE I

Bassam J. Judy
Govindan Chettur
Pemon J. Dihu
Mary Schuroer
Richard M. Snow

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

30 May 1983

Final Phase I Report for Period 1 July 1982-30 April 1983

Prepared for

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Edgewood Area
Aberdeen Proving Ground, Maryland 21010

The views opinions, and/or findings contained in this report are those of the author and should not be construed as an official Department of the Army position, policy or decision unless so designated by other documents.

The use of trade names in this report does not constitute an official endorsement or approval of use of such commercial hardware or software. This report may not be cited for purposes of advertising.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: DRXTH-TE-CR-83209	2. GOVT ACCESSION NO. AD-A129526
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Development of Chemical Processes for Chemical Demilitarization--Phase I	5. TYPE OF REPORT & PERIOD COVERED: Final Phase I Report 1 July 1982-30 April 1983
	6. PERFORMING ORG. REPORT NUMBER: IITRI-C06565
7. AUTHOR(s): Bassam J. Jody, Govindan Chettur, Remon J. Dihu, Mary Schurger, Richard H. Snow	8. CONTRACT OR GRANT NUMBER(s): DAAK11-82-C-0091
9. PERFORMING ORGANIZATION NAME AND ADDRESS: IIT Research Institute, 10 West 35th Street, Chicago, Illinois 60616	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: U.S. Army Toxic and Hazardous Materials Agency, Edgewood Area, Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE: 30 May 1983
	13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to U.S. Government Agencies only: ~~Research and Development~~ DE (April 1983). Other requests for this report must be referred to U.S. Army Toxic and Hazardous Materials Agency, ATTN: DRXTH-TE-D, Aberdeen Proving Ground, Maryland 21010.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Demilitarization, GB, VX, H, DF, Hydrolysis, Anhydrous Chlorinolysis, Hypochlorination, Acid Chlorinolysis, Pyrolysis, Treatment, Disposal

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report presents the results of a study to identify and evaluate potential chemical methods for the demilitarization of GB, VX, and H. Four concepts were identified as the leading candidates: anhydrous chlorinolysis, hot water hydrolysis, pyrolysis, and hypochlorination/acid chlorinolysis. Engineering and economic evaluations of the methods were conducted and the first two were recommended for laboratory testing. Both of these methods can convert the agents to chemicals that are useful to both the military and industry.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SUMMARY

The objective of this program was to develop state-of-the-art chemical processes and equipment designs suitable for incorporation into the design of full-scale chemical agents (GB, VX, H) and munitions demilitarization facilities. These designs would have the potential of converting the agents to useful products, reduce operating costs, conserve energy, and/or reduce capital investment when compared with the R&D baseline system. The results had to be demonstrated on a sufficiently large scale to prove feasibility and to provide design data for pilot scale systems.

The program was organized into two phases. The objective of Phase I, which is the subject of this report, was to identify, screen, and evaluate potential chemical methods for demilitarizing the three agents and to recommend the most promising methods for laboratory testing. The objective of Phase II is to experimentally test the recommended methods to verify theoretical expectations and to provide design data for pilot-scale testing of the leading method(s).

This program, conducted by IIT Research Institute, identified and analyzed methods that can save the Army up to about $450 million over the R&D baseline and convert agents to DF and other chemicals of great interest to the military and industry.

As part of Phase I we conducted a comprehensive search of the literature. We also contacted major chemical companies in the United States in order to identify all potential chemical methods that could convert the chemical agents to useful or at least environmentally benign compounds, at the least cost to the Government. Intensive in-house discussions were also held among our scientists and engineers as well as consultants with extensive experience in the chemistry of the agents, in an attempt to conceive other promising methods.

Our efforts succeeded in identifying over 25 methods, which were all screened by using quantitative criteria that we developed and refined specifi

cally for this program. Four methods were selected for engineering and economic evaluation:

(1) Anhydrous chlorinolysis
(2) Hot water hydrolysis
(3) Aqueous chlorinolysis and hypochlorination
(4) Pyrolysis.

A detailed process flow diagram was developed for each process, and mass and energy calculations were performed on these diagrams. The best available kinetic information and careful engineering judgment were used to size the equipment. Once the technical feasibility of a process was established, we evaluated its economics and compared the results with those for the R&D baseline. The economic evaluation addressed items such as installed cost of the equipment, labor, maintenance and spare parts, chemical feedstocks, disposal of by-products, and treatment of explosives and contaminated metals. The analysis also considered the value and marketability of the products.

The results of the engineering and economic evaluation were extremely encouraging. Anhydrous chlorinolysis and hot water hydrolysis were established as the two leading candidates. Both methods use commercially available equipment to convert the agents to useful chemicals with minimal waste by-products that can be easily disposed of.

Anhydrous chlorination can convert both GB and VX to DF, thus providing the Government with most, if not all, of the DF it needs for the next few years. It can also convert H to chemicals such as S_2Cl_2 which should be salable to industry. The net savings of this method over the baseline, including credit for DF, amounts to about $45 million per site or $450 million from all 10 sites.

Hot water hydrolysis also converts GB and H to chemicals that can be used by industry or by the military. It also convert VX to nontoxic water-soluble salts that can be transported by conventional means to waste management companies for incineration. The analysis showed that this method can save about $25 million per site over the baseline, or $250 million for all 10 sites.

The impressive results achieved with these two methods confirm that they deserve testing. We therefore recommend them for laboratory-scale testing as

Phase II of this program. The analysis done during Phase I identified areas where crucial information is lacking and can be generated only in the laboratory. The following points should be evaluated for both processes in Phase II:

(1) Identification of optimum operating conditions which could result in yet higher savings. These could be achieved via a carefully planned parametric study based on experimental data.

(2) Kinetic and vapor-liquid equilibrium data are lacking for both methods. These data are essential to size the equipment and to determine the final configuration of the flow diagrams.

(3) The strict purity requirements on some of the products, such as DF, requires proper purification techniques that need proving in the laboratory.

(4) Analytical methods for some of the products do not exist and need to be developed. This is especially true when solids and liquid mixtures are produced.

(5) Pollution abatement equipment that might be required for a full-scale plant needs to be identified and may be tested in the laboratory.

PREFACE

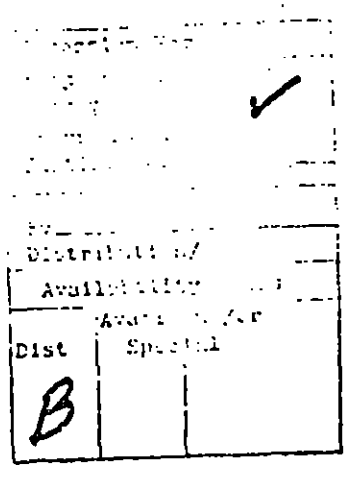
IIT Research Institute is very pleased to submit this final report on Phase I of Contract No. DAAK11-82-C-0091 (IITRI Project No. C06565) entitled, "Development of Chemical Processes for Chemical Demilitarization." This report includes technical and economic evaluations of many potential chemical methods that may be used to convert agents GB, VX, and H to reusable or environmentally safe products. As a result of these evaluations the two most cost effective methods are recommended for laboratory evaluation in Phase II. This report also includes a summary of the published literature on the chemistry of these three agents and a bibliography of 130 references.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Bassam J. Jody
Senior Engineer
Chemical Engineering Research

Approved by

Richard H. Snow
Manager
Chemical Engineering Research



CONTENTS

FIGURES

TABLES

TABLES (continued)

TABLES (continued)

1. INTRODUCTION

1.1 OBJECTIVE

The objective of this program was to develop state-of-the-art chemical processes and equipment designs suitable for incorporation into the design of full-scale chemical agents (GB, VX, H) and munitions demilitarization facilities. These designs would have the potential of converting the agents to useful products, reduce operating costs, conserve energy, and/or reduce capital investment when compared with the R&D baseline system. The results had to be demonstrated on a sufficiently large scale to prove feasibility and to provide design data for pilot scale systems.

The program was organized into two phases. The objective of Phase I, which is the subject of this report, was to identify, screen, and evaluate potential chemical methods for demilitarizing the three agents and to recommend the most promising methods for laboratory testing. The objective of Phase II is to experimentally test the recommended methods to verify theoretical expectations and to provide design data for pilot-scale testing of the leading method(s).

1.2 BACKGROUND

The Army has a need to dispose of large stocks of gradually deteriorating chemical warfare munitions, some of which are leaking. Processes have been developed for this purpose and are in operation at the Chemical Agent Munition Disposal System (CAMDS) pilot facility.

Although these processes work, they are labor intensive and costly. They use caustic to hydrolyze GB, incinerate the metals and explosives, and scrub the effluents. This procedure produces about 5 lb of salts per pound of GB destroyed. Although these salts contain less than detectable amounts of agents, they cannot be disposed of in an environmentally acceptable way because they contain sodium fluoride, phosphonates, and heavy metals; nor can they be placed in landfills without expensive precautions. Further, there is

the possibility that GB can be regenerated from these salts. The salts are therefore presently stored in drums, but the problem is not fully solved.

Acid chlorinolysis of VX, a method that does not directly produce salts, is practiced on a small scale. At CAMDS, however, alkali is used to treat the acid products and fix them into salt form. Incineration of H, the recommended method, not only produces salts, but also large quantities of SO_2 and HCl, which are costly to scrub.

Because of the salt problem at CAMDS and the high cost and low availability of the plant, the Army introduced a new concept which we will refer to in this report as the R&D baseline. The concept behind this baseline is to incinerate the agents, explosives, and metals after dismantling the munition to reduce the risk of explosions. The cost of building and operating the R&D baseline was determined for two scenarios:

(1) One centrally located large facility to which the agents will be transported

(2) Eight separate plants, one at each site. Two of these plants are double the size of each of the other six. Thus for discussion purposes it is looked upon as 10 sites with 10 small plants.

The Army also awarded contracts to different contractors to evaluate various mechanical methods to dismantle the munitions and to evaluate different thermal methods to demilitarize the agents. Each contractor must compare his findings with the R&D baseline. This report covers the progress achieved on Phase I of the chemical contract which was awarded to IITRI.

2. TECHNICAL PROGRESS

Phase I was organized into five separate tasks:

(1) Program Management and R&D Baseline Review and Analysis
(2) Literature Review
(3) Industrial Survey
(4) Concept Formulation and Evaluation
(5) Engineering and Economic Analysis and Reports.

The work performed and the results achieved on each of these five tasks are described in this section of this report.

2.1 TASK 1. PROGRAM MANAGEMENT AND BASELINE REVIEW AND ANALYSIS

2.1.1 Program Management

To properly manage the program, specific management tools were implemented. As a result, the progress of the work was satisfactory.

A detailed resource plan was developed that identified the effort that needed to be put on the program during each period. Three items were estimated: the progress needed during each period, the number of man-hours of each labor category required to perform the necessary duties, and the corresponding expenses. The resource plan was reviewed with the program manager at USATHAMA and adopted as a guideline for our progress.

Weekly review meetings were attended by all key program staff members to review progress and to address problems as they appeared.

Monthly review meetings were held with the program manager and his USATHAMA staff.

2.1.2 Baseline Review and Analysis

USATHAMA made available to IITRI a breakdown of the projected total cost of the R&D baseline. This information was reviewed with emphasis on how it relates to the chemical methods that might be identified in this program. We reached the following conclusions.

Siting. The total projected cost of a single site plant is about $101 million. If 10 such sites are required, the cost will be about $1.01 billion. The corresponding cost of a collocated site is $355 million. However, the cost of transporting the agents to the collocated site is $994 million. The single site is therefore more economical (by $339 million), assuming that the value of the money applied to the transportation cost is the same as that applied to the cost of building, providing equipment, and operating the single plants. Since the single site baseline appeared to be the leading competitor, our discussion here will be limited to it.

In addition, processes involving transportation of the agents are likely to be uneconomical. Conversion of the agents to non-surety materials and then transporting them to a collocated site could be competitive and deserves consideration.

Laboratory. The baseline is labor intensive. For short-term projects, such as the demilitarization of the agents, it makes good economic sense to operate with more personnel rather than to invest in costly automated equipment which will be used for a short period only. In case of an accident, however, this may present a safety problem.

Waste Disposal. The total cost presented for both the single site and the collocated site does not include the cost of disposing the waste products. The effluent from the incineration process will have to be scrubbed to remove traces of the agents and other harmful products. The scrubbing process will result in waste streams which have to be disposed of. Allowance was made, however, for storing the salts for extended periods of time.

Cost Comparisons. The cost estimates provided for the baseline system can be broken down into three main categories to facilitate comparison with other systems or methods:

- common cost, which includes all of the items that will be common to all possible methods and to the baseline such as security and safety related costs
- cost of munition disassembly, which will be common to many chemical methods and to the baseline
- method- or process-specific costs, such as the cost of incineration equipment in the case of the baseline system, and the cost of reactors in the case of chemical methods.

Costs associated with each of these categories may also be classified as facilities, equipment, and operating costs.

The corresponding values generated from the baseline are summarized in Table 1 below.

TABLE 1. BREAKDOWN OF BASELINE COSTS FOR A SINGLE SITE IN MILLIONS OF DOLLARS

Item	Total for Baseline, $	Munition Common Cost, $	Process Disassembly Cost, $	Specific Cost, $
Facilities	7.38	3.97	1.98	1.43
Equipment	34.70	10.44	2.83	21.44
Operation	59.16	44.07	4.82	10.26
Totals	101.24	58.48	9.63	33.13
% of Total	100	58	9	33

Details of the breakdown for each cost item are given in Tables 2, 3, 4, and 5.

Cost Breakdown. The common cost constitutes 58%, followed by the process-specific cost which makes up 33% of the total cost. The process-specific cost is the area in which major improvements in cost can be made.

Process Availability Savings. Increased process availability would decrease the common operating cost, which is about 44% of the total cost. Availability of the baseline plant ranges from 48% in the case of the mortars to 66% for the rockets and mines, with an overall availability of about 60%. Increasing that availability will reduce the required time for demilitarizing the stockpiles and thus reduce common cost items such as labor associated with security, administration and monitoring, and certain safety items.

Munition Disassembly Savings. Munition disassembly cost is only 9% of the total. Since this section has the least availability, it may be economical to have two of these in parallel in order to increase the overall availability of the demilitarization plant. This will reduce common operating costs.

Operating Time. The baseline is estimated to operate 20 hours per day and 250 days per year.

TABLE 2. BREAKDOWN OF FACILITIES COST FOR SINGLE-SITE R&D BASELINE SYSTEM

Item	Total Baseline ($)	Common ($)	Munition-Disassembly ($)	Process Specific ($)
Facilities				
Unpack area	118,800		118,000	
Vestibule	35,000	35,000		
RMDLWE area	528,000			528,000
Glove box room	132,000		132,000	
Explosive containment room #1	420,000		420,000	
Explosive containment room #2	420,000		420,000	
Explosive containment room prts/sumps	11,700		11,700	
PBIF area	236,700			236,700
Bulk item room	29,700			29,700
Central control room	132,000	132,000		
Chem. storage and dist.	47,700	47,700		
Life support area and suit up	118,800	118,800		
Toxic maint. area	29,700	29,700		
Motor control ctrs	22,500	22,500		
Projectile demil bay	44,100		44,100	
Toxic cubicle	71,100	71,100		
Scrap handling	133,200			133,200
In-plant office	59,400	59,400		
Air locks and corridors	369,000	369,000		
HVAC	36,000	36,000		
Conveyors	372,600		372,600	

TABLE 2. BREAKDOWN OF FACILITIES COST FOR SINGLE-SITE R&D BASELINE SYSTEM (continued)

Item	Total Baseline ($)	Common ($)	Munition-Disassembly ($)	Process Specific ($)
Monitoring	22,700	22,700		
Power packs, controls, reservoir	36,000	36,000		
Bldg sub-total	3,427,700	980,900	1,519,200	927,600
Laboratory	173,250	173,250		
Personnel support	660,620	660,620		
Bldg sub-total	4,261,570	2,065,570	1,268,400	927,600
Medical bldg	187,440	187,440		
Supply/parts warehouse	269,780	269,780		
Salt and drum storage	150,880			150,880
Nontoxic maint.	81,840	81,840		
Engineering/adminis.	310,590	310,590		
Guard house	38,800	38,800		
Utility bldg	122,140	122,140		
Pads	14,500			14,500
Transport/holding igloo	157,080	157,080		
Security fence	63,040	63,040		
Sub-total	5,657,660	3,045,480	1,519,200	1,092,980
Other support [12%]	678,919	365,457	182,304	131,158
Const. supervision [6-1/2%]	411,878	221,711	110,598	79,569
Design [10%]	633,658	341,094	170,150	122,414
Grand Total	7,382,115	3,973,742	1,982,252	1,426,121

Capital Equipment	Total Baseline ($)	Common ($)	Munition-Disassembly ($)	Process Specific ($)
Vestibule (lockers)	263,160	263,160		
ROTARY furnace	7,000,000			7,000,000
Air heat exchanger	80,000			80,000
Glove box room	190,790		190,790	
Explosive containment #1				
Rocket shear	88,820		88,820	
Mine punch .	151,320		151,320	
Burster shear	85,530		85,530	
Explosive containment #2				
Mortar and reverse ass'y	289,470		289,470	
Proj. bulk item furnace area	9,000,000		151,320 (1)	8,848,680 (1)
Air heat exchanger	95,000			95,000
Press and plug mech. etc.	157,890			157,890
Central control room	796,050	796,050		
Chemical storage and distribution	723,680	723,680		
Life support	401,320	401,320		
Toxic maint. area	26,320	26,320		
Air locks and corridors	986,840	986,840		
Motor control center	230,260	230,260		
Proj. demil bay	350,000		350,000	
HVAC	1,171,050	1,171,050		
Hydraulic - Power packs	276,320		276,320	
Valves, pipes, fittings	144,470		144,470	
Laboratory GC etc.	289,470	289,470		
Personnel support	51,910	51,910		
Medical	200,000	200,000		
Supply/parts warehouse	22,000	22,000		
Office equipment	70,000	70,000		
Drum storage	22,000			22,000
Nontoxic maintenance	52,630	52,630		
Engineering/Administration	78,950	78,950		
Laundry	78,950	78,950		
Utility bldg (generator/boilers)	657,890	657,890		
Pads (spray dryer and drumming)	250,000			250,000
	295,000			295,000
	14,470			14,470
	130,000			130,000
	170,000			170,000
Fuel Tanks	34,000	10,840 (2)		25,150 (2)
Decon tanks	54,000	54,000		
Air filtration	690,790	690,790		
Transport/holding inloo	22,000	22,000		
Other eq. CC-TV	263,160	263,160		
Scty radio and detector	197,370	197,370		
Communication	52,630	52,630		
Toxic Cubicle	32,890	32,890		
Residue handling	65,790			65,790
M - monitors	424,000	424,000		
C - conveyor/hoists	513,160		513,160	
Total	27,764,340	8,349,160	2,761,200	17,553,980
Design cost 25%	6,941,085	2,087,290	565,300	4,288,495
Grand Total	34,705,425	10,436,450	2,826,500	21,442,475

1. $151,320 for bulk item puncture, same as mine punch machine.

2. Ratio is based on fuel consumption.

TABLE 4. BREAKDOWN OF LABOR COST FOR A SINGLE-SITE R&D BASELINE SYSTEM

	Total Baseline Labor Man year/year Munition Type A	A/C	D	Common Total Man Year	Munition Disassembly Total Man Year	Process Specific Total Man Year
Labor						
Unpack area	18	24	6		18(.91) + 24(1.7) + 6(.37) = 59.6	
RPLME furnace	9	9	3			9(.91) + 9(1.7) + 3(.37) = 24.60
Munition processing bay		3				
Explosive containment Rm #1	3	3			3(1.7) = 5.1	
Explosive containment Rm #2		3			3(.91) + 3(1.7) = 7.83	
Projectile/bulk furnace area		9	9		3(1.7) = 5.10	
Central control room	12	12	12	12(.91) + 12(1.7) + 12(.37) = 35.76		9(1.7) + 9(.37) = 18.63
Life support	12	12	12	12(.91) + 12(1.7) + 12(.37) = 35.76		
Air locks and corridors		6		6(1.7) = 10.20		
Laboratory and monitoring	24	24	24	24(.91) + 24(1.7) + 24(.37) = 71.52		
Personnel support	3	3	3	3(.91) + 3(1.7) + 3(.37) = 8.94		
Medical	6	6	6	6(.91) + 6(1.7) + 6(.37) = 17.88		
Warehouses	12	12	12	12(.91) + 12(1.7) + 12(.37) = 35.76		
Engineering/Adm/Maint	24	24	24	24(.91) + 24(1.7) + 24(.37) = 71.52		
QA/operation staff (2)	12	12	12	3(.91) + 3(1.7) + 3(.37) = 8.94	3(.91) + 3(1.7) + 3(.37) = 8.94	6(.91) + 6(1.7) + 6(.37) = 17.88
Laundry	6	6	6	6(.91) + 6(1.7) + 6(.37) = 17.88		
Guard force	9	9	9	9(.91) + 9(1.7) + 9(.37) = 26.82		
Utility	3	3	3	3(.91) + 3(1.7) + 3(.37) = 8.94		
Spray dryer dumping	6	6	6			6(.91) + 6(1.7) + 6(.37) = 17.88
Maintenance	19	19	19	19(.91) + 19(1.7) + 19(.37) = 56.62		
Total man year/year	178	205	166	406.54	44.37	78.99

TABLE 5. BREAKDOWN OF LABOR COST FOR A SINGLE-SITE R&D BASELINE SYSTEM

	$/year	Total Baseline ($)	Common ($)[1]	Munition Disassembly ($)[1]	Process Specific ($)[1]
Total labor cost (see III.A)		28,595,000	20,327,000	4,318,500	3,949,500
Equipment acceptance labor[5]		1,700,000	1,700,000		
Training and systems labor[6]		5,125,000	5,125,000		
Change out A→B/ and B/C→D Type[7] (10 + 250,000 and 8,300,000) + 0.17		3,153,500	3,153,500		
Shutdown labor[8]		1,700,000	1,700,000		
Refractory change labor		204,000			204,000
Other Direct Costs					
Equipmepnt acceptance		829,429	829,429		
Training and systems		1,244,157	1,244,157		
Change out other direct costs (2,488,313 + 2,488,313)+.17		846,026	846,026		
Shutdown		829,429	829,429		
Refractory change		99,531			99,531
Other Annual Direct Costs[3]					
Water					
RMLDWE scrubber	1,908	5,686			5,686
PBIF scrubber	3,180	9,476			9,476
Other	1,272	3,791	3,791		
Electric					
RMLDWE furnace	11,500	34,270			34,270
RMLDWE heat exchanger	5,500	16,390			16,390
RMLDWE scrubber	17,500	52,150			52,150

TABLE 5. BREAKDOWN OF LABOR COST FOR A SINGLE-SITE R&D BASELINE SYSTEM (continued)

	$/year	Total Baseline ($)	Common ($)[1]	Munition Disassembly ($)[1]	Process Specific ($)[1]
RMLDWE salt equipment	23,000	68,540			68,540
PBI furnace	19,000	56,620			56,620
PBI heat exchanger	9,500	28,310			28,310
PBI scrubber	28,500	84,930			84,930
PBI salt equipment	38,000	113,240			113,240
Other	152,500	454,450	454,450		
Fuel Oil					
RMLDWE furnace	146,400	436,272			436,272
PBI furnace	240,000	715,200			715,200
Other	166,800	497,064	497,064		
Spare Parts (62, capital equipment)	2,082,326	6,205,332	1,866,037	505,378	3,833,915
Materials and supply					
RMLDWE furnace	70,000	208,600			208,600
PBI furnace	115,000	342,700			342,700
Other[4]	1,384,239	4,125,032	4,125,032		
Services	460,500	1,372,290	1,372,290		
Total Operating Costs		59,156,415	44,073,205	4,823,879	10,259,331

[1]Man-year is calculated by multiplying No. man year/year x production year for this type munition (production years category A = 0.91; category B/C = 1.7; Category D = 0.37).
[2]The labor is proportioned with capital equipment cost with not less than 3 people for 3 shift operation.
[3]Cost = cost/year x 2.98 years (total production years).
[4]This number could not be substantiated from given data; used as is.
[5]Cost = cost/year x 0.5 years (non-productive years).
[6]Cost = cost/year x 0.5 years (non-productive years).
[7]Cost = cost/year x 0.17 years (non-productive years).
[8]Cost = cost/year x 0.06 years (non-productive years).

The above breakdown made it easier to compare the different chemical methods with the R&D baseline as shown under Task 5 of this report.

In addition to evaluating the R&D baseline, two engineers from IITRI visited CAMDS after reviewing the series of reports entitled, "Operation of the Chemical Agent Munitions Disposal System (CAMDS) at Toole Army Depot."[1] The purpose of the visit was to see and assess the state of the art in chemical agent demilitarization, since CAMDS is the largest facility for this purpose.

From the review of the CAMDS report, the site visit, and the discussion we had with the cognizant staff members, we made the following observations:

Safety Operations. CAMDS has been operated safely since its startup in 1976. No chemical injuries occurred to the employees during that period. Consequently, its procedures for safe handling and operation should be adopted as a basis for setting standards, although modifications might be required to reflect the improvements in technology since it was designed.

Level of Technology. CAMDS technology is not state of the art even though it involves many nonconventional components and subsystems.

Processing of Agent. Processing of GB results in large amounts of salts which could not be disposed of by conventional means. Reprocessing of the salts is required before final disposal can be achieved. Reformation of GB from the salts is possible.

Utility Requirements. Utility requirements are excessive, making the operating cost of the facility high. This is especially true in the case of steam and electric power.

Maintenance. Maintenance costs and downtimes are also excessive. This is at least partially due to the complicated design of the machinery involved in munition disassembly.

2.2 TASK 2: LITERATURE SEARCH

In order to identify potential chemical methods and to avoid duplicating work done by others, it was essential to review reports and articles prepared on the subject. A computer-aided search of literature was initiated with the

aid of search specialists. Four groups of keywords were identified. Group A consisted of primary keywords:

- Chemical Warfare Agents
- Nerve Agents
- Nerve Gas
- Mustard Agent
- Toxic Agent
- Chemical Weapons
- Military Chemical Agents
- GB Agent
- DF Agent
- H Agent
- Nivalenol
- Phosphate
- Phosphonic Acid
- Sarin
- Organophosphorus
- Difluoro
- HD Agent
- VX Agent
- DFP Agent
- Fluoropnosphonate

Group B was labeled "Engineering Perspective" and included the following terms:

- Mechanism
- Product
- Preparation
- Demilitarization
- Destruction
- Neutralization
- Separation
- Synthesis
- Manufacturing
- Decontamination
- Disposal
- De-activation
- Conversion

Group C was labeled "Chemical Perspective" and included the following terms:

- Reaction
- Ozonation
- Fluoridation
- Hydrolysis
- Properties
- Photolysis
- Oxidation
- Pyrolysis
- Reduction
- Chlorination
- Catalysis
- Isomerization
- Halogenation

Group D included only one keyword, "Incineration." This was done for the purpose of excluding articles on incineration.

The following data systems were interrogated using the four groups of keywords:

- Dialog Information Retrieval System, which includes the following data bases: NTIS, CIN, ENVIROLINE, SSIE, EI, Pollution, CA (all files) and APTIC
- SDC (System Development Corporation), which includes the following data bases: Safety and USCA
- DOE/RECON, which was used to access "Research In Progress Files."

A logic for the research strategy was then established using the four groups of keywords. The following logic statements were executed:

Groups (A&B) (for Engineering Index only)

Groups (A&C) (for Chemical Abstracts only)

Groups (A&B) + (A&C) for all other bases

All statements excluded articles on incineration. The first statement formed pairs from groups A and B. The second statement formed pairs from groups A and C and exluded both D and B terms in order to eliminate some of the duplications. The total of 2088 articles and abstracts was identified by the computer search using the above strategies.

Each of the abstracts was reviewed, and over 300 pertinent articles and reports were ordered so that they could be studied in detail.

In addition, local libraries were visited in order to obtain the interesting articles directly. A search was also conducted of the Chemical Systems Laboratory (CSL) library for classified work. Interestingly, little classified literature was discovered that advanced our knowledge about the subject.

Two consultants were also hired to help us find pertinent information that might not be available through the means discussed above, as well as to obtain a first-hand understanding of the chemistry involved. The consultants were Dr. Joseph Epstein, a former CSL employee and Dr. Kenneth De Bruin, professor of organophosphorus chemistry at Colorado State University.

A summary of our findings from the literature search is presented in Appendix A in two sections. The first section discusses the electronic structure and bonding of the agents; the second section addresses potential reactions for their demilitarization.

The following general observations on literature were made:

(1) The literature on GB is fairly extensive. Data were found on the kinetics of several reactions involving GB. Data concerning the properties of GB were also available. More experimental work was done on GB than on the other two agents.

(2) Data on VX are scarce and of little use as far as this work is concerned, except in the chlorinolysis of VX.

(3) Data on H are scarce. However, good and pertinent information was uncovered in articles published as early as the 1920s.

(4) The literature has little valuable data on the impurities in the agent-containing munitions and on the chemical and physical changes that the agent might have undergone.

(5) Analytical methods for the agents and their reaction products are not very well developed, especially for solid and liquid mixtures. Extensive work is needed to develop such methods.

2.3 TASK 3: INDUSTRIAL SURVEY

The objectives of Task 2 were to:

(1) Identify chemical processes not available in the literature but that could be developed or that are under development by industry and might be applicable to the demilitarization of agents

(2) Identify chemical compounds that could be derived from agents and that industry would be interested in procuring for their operations.

To achieve the first objective, an advertisement was published (17 September 1982) in the "Commerce Business Daily" requesting information on potential processes or methods. Sixteen organizations sent information describing methods or ideas for demilitarization (Table 6). Three of the methods proposed were thermal methods and thus were not considered further. Other organizations responded by providing description of capabilities but no specific methods or ideas.

To identify target compounds of interest to industry, major chemical companies in the United States were contacted by telephone and by letter. Using the 1982 Chemical Engineering Catalog, a list was compiled of the chemical companies whose stated products were agricultural chemicals, including insecticides and pesticides, flame retardants, plasticizers, or

surfactants. The manager of commercial development, R&D director, product manager and/or purchasing agent of the larger chemical companies was contacted.

TABLE 6. SUMMARY OF RESPONSES TO ADVERTISEMENT IN CBD

Company/Corporation	Person	Method/Remarks
ROHM and Haas Co.	R. M. Kopchik	Sorbent and reactive resins
Ion Physics	R. D. Evans	Irradiation with high energy electrons
Franklin Research Inst.	L. L. Pytlewski	Use of NaPEG™ reagents
Westgate Research	L. G. Cole	Ozone and UV
Giner	J. Giner	Electro oxidation/reduction
Wilson Labs	R. P. Selm	Photolytic oxidation
EG & G	J. H. Wolfram	Biological methods
IT Enviroscience	J. H. Exner	Photolysis, catalytic wet oxidation, chemical reduction
Maxwell Labs	F. Painchaud	Flashblast-intense pulses of light
University of Dayton	B. Dellinger	Thermal
Projinex	J. T. Enders	Thermal
Applied Energetics	J. B. Dicks	Thermal
Innova	R. Budin	Electric fields (polarize particles and produce hydroxyl radicals and ozone
Energy and Environment	J. H. Porter	Thermal
Sumx Corp.	D. W. DeBerry	Ozone and UV
Wilson Labs	R. P. Selm	Photolytic oxidation

Initially, the subject matter was discussed vaguely, and if the contact was interested, the origin of the material was revealed. None of the contacts seemed to be overly concerned about the origin of the products. The contacts were asked:

- If they were using compounds that we thought could be produced from the agents.
- If they had any future plans to use them.
- If they would be interested in using some intermediates if they became available at minimal cost.

Most companies wanted to see something in writing in order to evaluate this opportunity. They were interested in the quantities, purities, availability, processing rates, and toxicities of the proposed compounds. A letter to that effect was mailed to them. The chemical companies that were contacted are listed in Table 7. Companies to which letters were mailed and their responses are summarized in Table 8.

Overall, the industrial search was successful. Findings from the survey are as follows:

(1) Several compounds that are of interest to industry may be derived from the agents in the desired purity. These include HCl, HF, divinyl chloride, tetrahydrothiophene, dichloroethane, and ethylene.

(2) Items of concern to some of the companies are:

- quantities available and delivery rate
- impurities that might affect the quality of their final products. While the source of the chemical was not a major concern for some of the companies, it could be among the reasons that caused others not to be interested.

(3) The market value of such chemicals constitutes only a small portion of any demilitarization plant. In some cases, however, the savings from not having to dispose of the intermediates from which these chemicals are derived are substantial.

(4) Responses to our advertisement in the Commerce Business Daily produced several potential methods which were screened along with those identified in the literature and from our in-house efforts.

(5) Valuable information was gathered through our industrial contacts about disposal methods and costs of by-products of the chemical methods.

2.4 TASK 4: CONCEPT FORMULATION AND EVALUATION

This task also had two main objectives:

(1) Identify novel concepts not discussed before

(2) Establish kinetic information for leading processes so that they could be evaluated in engineering and economic terms.

To achieve the first objective, intensive in-house discussions involving chemists and chemical engineers were carried out. Two consultants, Dr. Joseph Epstein and Dr. Kenneth DeBruin, were also invited for several sessions to

TABLE 7. INDUSTRIAL SURVEY--INITIAL TELEPHONE CONTACTS

Company	Person Contacted/Title	Phone No.	Response
International Mineral and Chemicals Mundelein, Ill.	Paul Riech Corp. Purchasing Agent (Chemicals)	312/761-9800	They do not use any organophosphorus compounds. They use some HF and monoethanolamine.
Dearborn Chemicals Lake Zurich, Ill. (misc. chemicals)	R.T. Philmer Corp. Purchasing Agent	312/438-9800	They use some HCl, no organophosphorus compounds.
Mallinckrodt Calsicat Division Erie, Pa. (misc. chemicals)	R. Hubert Material Manager	814/455-0951	This division uses large amounts of phosphoric acid, and some HCl, they generally will not use recycled or recover products because in the catalyst manufacture (in which this division is involved), very high purity reagents are required and trace amounts of metals act as poisons to the catalyst material.
Mallinckrodt St. Louis, Mo. (fungicides)	R. Whorton Corp. Purchasing	314/895-2045	They buy sodium and calcium phosphates, some organophosphorus compounds. They have a need for HCl, HF, and MEA, and will if economically justifiable, purchase recovered acids.
Monsanto St. Louis, Mo. (flame retardants)	Henry Harris Product Manager Flame Retardants	314/694-1000	The commodity they are shooting for in flame retardants is aminomethyl phosphonate. They will take, for example, a PCl and convert it to a phosphonate. He thought there were some possibilities in the compounds we mentioned, but referred us to someone in their corporate office that is in charge of reprocessing some of their waste materials.
Olin Chemical Stamford, Conn. (flame retardants, pesticides, etc.)	Mr. Bessler Corp. Purchasing Agent	203/356-2000	They do not purchase any organophosphorus compounds, he suggested that we send him a letter with the chemicals and their specifications and they will determine any usages for them.
Velsicol Chemical Chicago, Ill.	Mr. Stevens Chemical Purchasing Agent	312/670-4500	They use one organophosphorus compound, that is CECPT, diethylchloroprosphonothionate, used in the manufacture of diazonin. They purchase this from either Stauffer or Ethyl. He does not feel that a recycled material could be used in pesticide manufacture because they are required to submit to the EPA a confidential listing of the components in the pesticide. If a recycled material is to be used as a raw material, the exact composition would have to be determined.
Stauffer Chemical Hyala Farm Rd. Westport, Conn. 06881	Mike Silvon Commercial Development Intermediates	203/222-3000	Stauffer routinely recovers organophosphorus compounds. They are set up to do chemical conversions with pyrolysis. They recover phosphorus for use in fertilizers. We read him some of the compounds (byproducts) that we expect to get and he said that he could see a use for a couple of them as intermediates. He would like me to send him a letter with the list of compounds possible, their volumes, the timing for processing of the compounds, purity or concentrations, economics (i.e., cost of material) and toxicity of mixtures. If there is enough of the material, and they could see some profit from processing the organophosporus wastes, they would be willing to take them.
American Cyanamid 1 Cyanamid Plaza Wayne, N.J. 07470	John Banger Phosphate and Metals Recovery	201/831-2000	They manufacture triethyl phosphate oxide. This division does not do any waste recovery, but he feels that some people in his company may be interested in this possibility. He wants us to send him a letter outlining what we are trying to do and he will circulate this letter around his division and the agricultural chemicals division.
(Hooker) Chemical Occidental Chemical P.O. Box 728 Niagara Falls, N.Y. 14302	Bob Zielinski Commercial Development.	716/278-7777	They do not routinely process organophosphorus compounds. We read off some of the compounds from the CM reactions and he said they may have a need for some of them in some new products that they are trying to develop. He was still interested when we told him the nature of the compounds. He would like a letter describing what we are trying to do, the compounds we are trying to produce, quantities, etc.
Dow Chemical Midland, Mich.	Jack Ementrout R&D Marketing	517/636-1000	They purchase organophosphorus and sulfur intermediates very little, manufacturing them on their own; therefore, there does not seem to be any interest on their part. He suggested some uses for organophosphorus compounds as in flame retardants, agricultural chemicals, plasticizers and insecticides.

TABLE 7. INDUSTRIAL SURVEY—INITIAL TELEPHONE CONTACTS (continued)

Company	Person Contacted/Title	Phone No.	Response
Ethyl Corp. P.O. Box 341 Baton Rouge, La. 70821	Roger Moser Vice President, R&D	504/359-7171	They have some interest in obtaining organophosphorus or organosulfur compounds; however, they have certain purity requirements. He would like some more information, i.e., the types of compounds, the source, etc.
Pennwalt, Inc. 3 Parkway Philadelphia, Pa. (Mercaptans, eg. Chemicals, etc.)	Frank Dougherty Organics Division (Product Manager)	215/587-7150	Other divisions may be interested in obtaining the organophosphorus and organosulfur compounds. They would like a letter with a list of the chemicals, and information on purities, the volumes (whether a commercial venture is anticipated), and explanation of the program at IITRI and when these commodities would be expected to become available. He said that he would circulate the letter to other divisions that may have an interest in these compounds.
Merck & Co. Merck, Sharp and Dohme Research Lab. Hillsborough Rd. Three Bridges, N.H. 08887	Richard Dyas Research and Development	201/369-3001	He requested a letter with any information we may have on the chemicals. He would pass on the letter to the various divisions.
Ashland Chemical P.O. Box 2219 Columbus, Ohio 43216	Larry Baker Planning and Development	614/RR4-4683	He would like us to send him a letter with any information about the chemicals that we may produce. He is uncertain about the application of organo-P,S compounds within Ashland.
Sherex Chemical Co., Inc. P.O. Box 646 Dublin, Ohio 43017	Richard Dodwell Mgr., Commercial Development	614/764-6500	They manufacture ester plasticizers, and mine phosphorus. He was not sure of a need for these chemicals off-hand; however, he said he would pass a letter around for us if we sent it.
Mobil Chemicals P.O. Box 2583 Richmond, Va. 23261	Andy Bladon Commercial Development	804/788-4291	They manufacture intermediates for pesticides etc. He was not very optimistic, but would like to see the letter anyway.
Mobay Chemicals Parkway West Pittsburgh, Pa. 15205	Howard Martin Corporate Planning	412/777-2727	Their main interest in organophosphorus, organosulfur compounds was as intermediate for agricultural chemicals. He was interested in receiving our letter describing the process.
E.I. Dupont de Nemours Wilmington, Del. 19898	C.R. Whitcombe M&L Dept.	302/744-4562	He was interested, though noncommittal. He would like a list of the chemicals.
Air Products and Chemicals P.O. Box 538 Allentown, Pa. 18105	Joseph Santangelo Mgr. Business Development	215/481-6958	He said there may be some interest in the Polymer/chemical group and suggested that I send the letter to Dr. Terry J. Wharton, the Research Director for that that group.

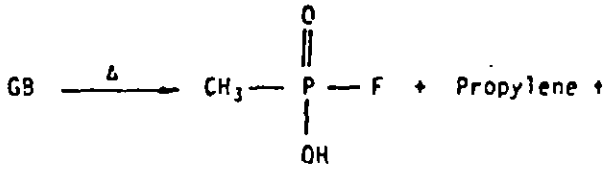
TABLE 8. INDUSTRIAL SURVEY--SUMMARY OF RESPONSES

Company	Means of Contact	Response
Air Products	Letter	No interest
Pennwalt, Corp.	Letter	Interested in tetrahydrothiophene (sent spec sheet)
Olin Chemicals	Letter	No interest
Mobay Chemical	Telephone	Interested in hydrogen chloride, 1,2-dichloroethane, and vinyl chloride (sent spec sheets)
American Cyanamid	Telephone	Still under evaluation, no interest at time of call.
Mobil Chemicals	Telephone	No interest
Merck & Co.	Telephone	No interest; however, if more compounds were added to the list he would consider them.
Ethyl Corp.	Telephone	Letter has been evaluated by Detroit office. The general recommendations involved the use of the chemicals on the list for phosphorus-based insecticides and other proprietary chemicals.
Sherex Chemical	Telephone	No interest
Hooker Chemical Occidental	Telephone	Minor interest in HF and polymeric phosphorus. If more specific information becomes available, they would reevaluate.
Stauffer Chemical	Telephone	Evaluated the letter, but do not at the present time have a clear fit for the chemicals. The potential was for phosphorus-containing fertilizers. They would be able to handle the products as wastes, however. In their Mt. Pleasant facility they use organophosphorus wastes as a fuel source in their basic phosphorus plant; these wastes also include sulfur-containing wastes. They also generate organophosphorus and sulfur wastes at this facility. They incinerate these and recover HCl and phosphoric acid. Incinerator effluents are all combined and go through an SO_2 scrubber. The contact person for arranging waste disposal is Mr. Mike Silvon.
Ashland Chemical	Letter	Reviewed by about 10 people. They may have had some use for these; however, the amount of processing they may have to do to use the chemical, plus the uncertainty as to the availability and quantity of the compounds, made them conclude that it was not worth their while to spend time considering this further.

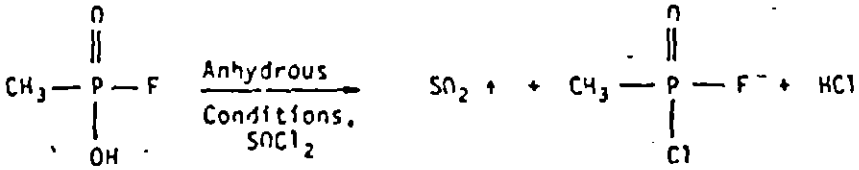
help the in-house staff identify and assess all possible opportunities. As a result, the following possible reactions were identified, which, to the best of our knowledge, are not discussed as such in the literature for large-scale chemical demilitarization. These are:

- Anhydrous chlorinolysis of GB and VX to produce DF
- Reaction of mustard with sodium metal to produce sulfolane solvents
- Reaction of agents with hydrogen and hydride ions
- Conversion of agents to waste for eventual disposal as nonsurety materials
- Chemical decontamination of containers to replace incineration.

Anhydrous Chlorination of GB to Produce DF. The process may be summarized by the following sequence of reactions[2-6]:

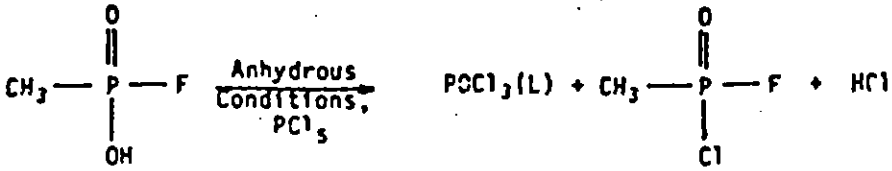


Methyl Fluorophosphonic Acid (MFPA)

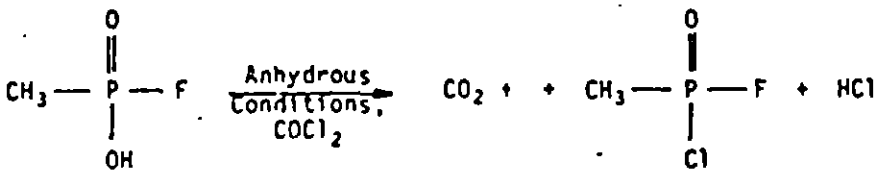


MFPA

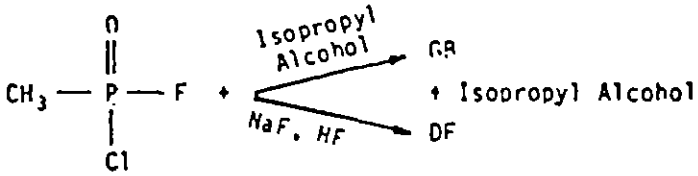
Methylchlorofluorophosphine oxide (MCFPO)



Phosphorous oxychloride

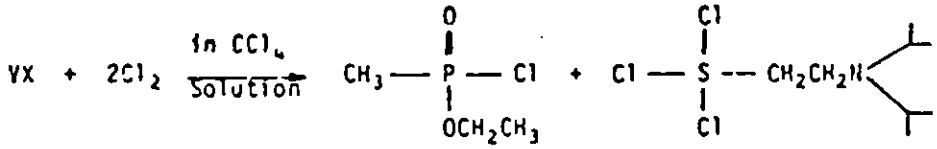


Methylfluoro
chlorophosphine oxide



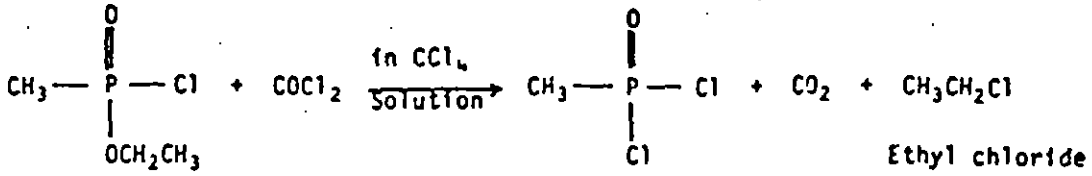
The propylene may be used as a fuel to supply heat for the controlled pyrolysis shown in the first of these reactions.

Anhydrous Chlorinolysis of VX to Produce DF. This process may be summarized by the following sequence of reactions[4-6]:

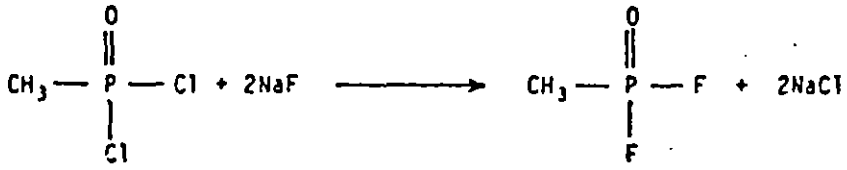


O-Ethyl methyl
phosphono chloridate

N,N-Diisopropyl aminoethyl
sulfur trichloride



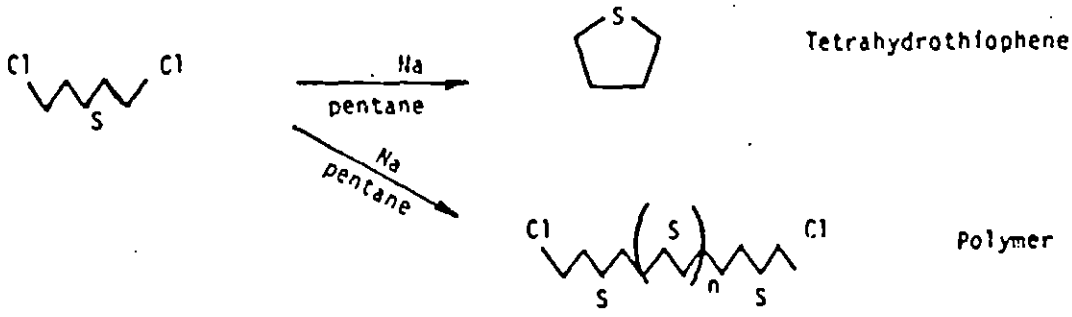
Methyl dichloro-
phosphine oxide



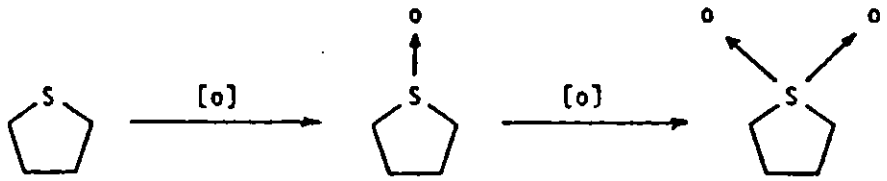
DF

The above two methods were screened and found very promising. Therefore we conducted engineering and economic analyses of both methods. Our analyses also showed that anhydrous chlorination of H is a viable method to produce $ClCH_2\text{-}CCl_3$, S_2Cl_2, and HCl, all of which are marketable products.

Reaction of Mustard with Sodium Metal to Produce Sulfolane Solvent (Wurtz Reaction).[7,8] Under dilute conditions, cyclization of mustard to tetrahydrothiophene would be favored, while in concentrated solutions of mustard, polymerization would be more likely to occur, as shown below:



Should cyclization to tetrahydrothiophene be the favored reaction, then it would be possible to obtain some useful products from this reaction, in particular, tetrahydrothiophene sulfoxide or tetrahydrothiophene sulfone (sulfolane), the latter of which is used as a solvent in the chemical industry.

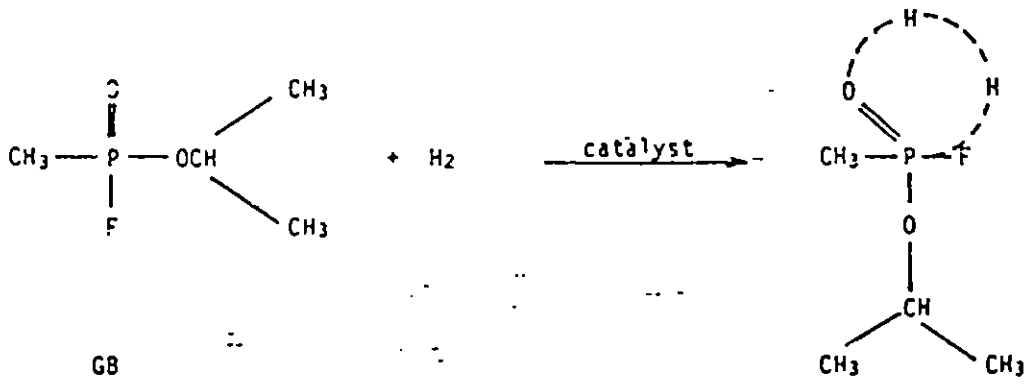


Tetrahydrothiophene oxide

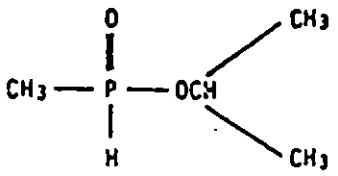
Sulfolane

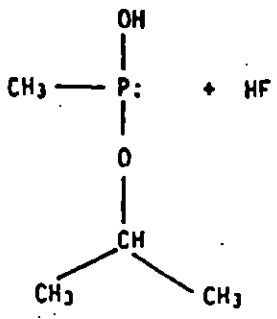
This method was screened. However, the lack of information on the likelihood that these reactions would proceed and only slight industrial interest in the product suggested that this method does not warrant engineering and economic evaluation. It is presented here so that if more information becomes available in the future the Army could re-evaluate it.

Reaction with Hydrogen and Hydride Ions. This process may be summarized by the following sequence of reactions which are highly speculative:[9]



GB

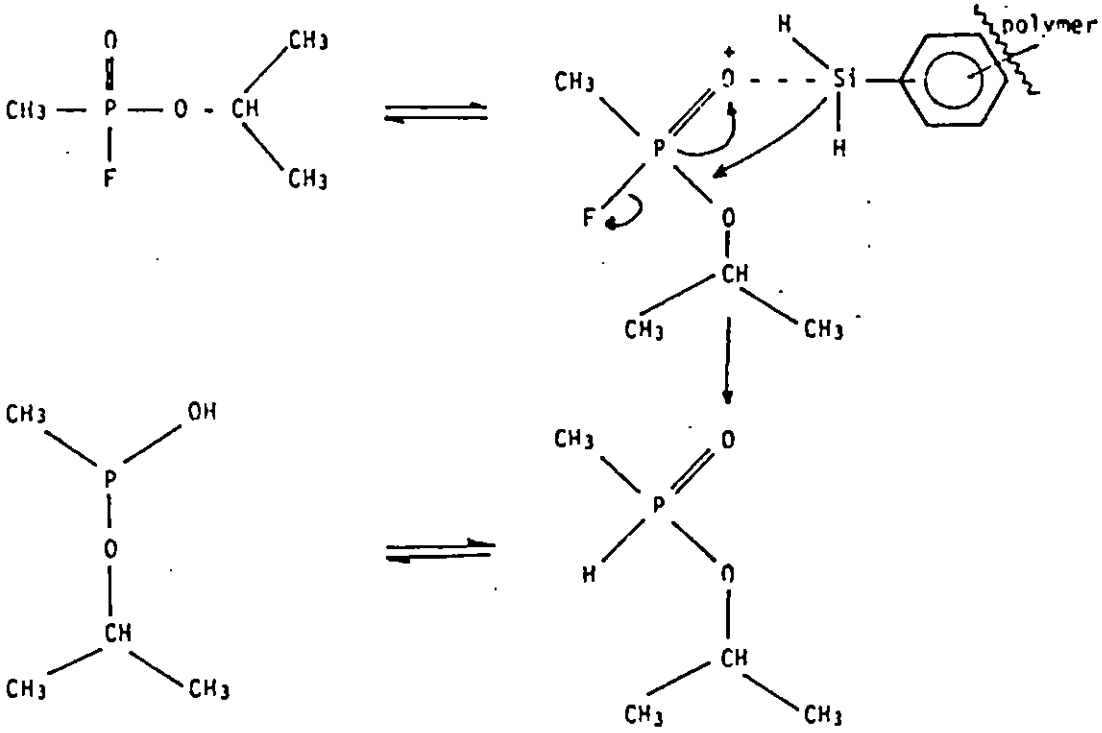




O-isopropyl methyl phosphite

The production of HF is a serious problem because it will attack the catalyst.

A similar reaction for VX could also be possible. However, the sulfur in VX will also poison the hydrogenation catalyst. In the case of GB, the formation of HF can be avoided by using hydride ions instead of hydrogen. This will produce fluorine ions instead of HF,[9] i.e.:

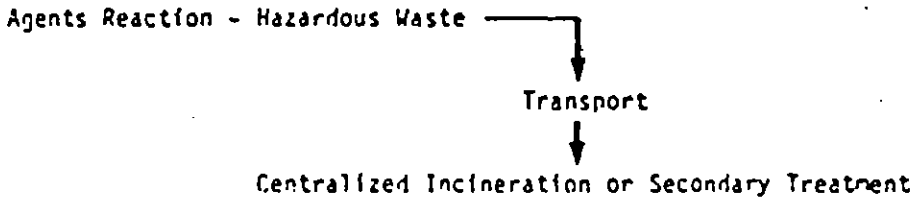


O-isopropyl methyl phosphite

The above reactions are envisioned because transformations involving P=O and P-C bonds are the most difficult to achieve. If the P=O bond is removed, the phosphorus becomes tri-coordinated and forms substituted phosphines.

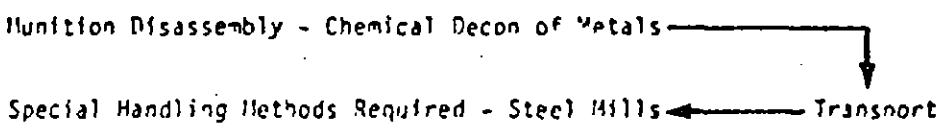
As stated earlier, these reactions are highly speculative, especially the reaction with hydrogen. Lithium aluminum hydride, however, was found very helpful for the preparation of phosphines from compounds such as alkyl dichloro phosphine oxide and dialkyl esters of aryl phosphonic acid.[10,11] Cyclohexyl phosphine has also been prepared from cyclohexyl dichlorophosphine oxide using sodium dispersion in toluene at 90°C.[10] The phosphines are highly toxic,[12,13] poisoning the nervous system.

Conversion of Agents to Waste Grade in a Simple and Economic Process.



Hydrolysis and pyrolysis were considered as possible reactions. Both alternatives were evaluated and the results are discussed in Section 5.

Chemical Decontamination of Metallic Containers to Replace Incineration.



This method is discussed in Section 5.

Anhydrous chlorination of GB and VX to produce DF was found to be one of the two best chemical methods which we are recommending for laboratory testing. The other method is hot water hydrolysis, which was also conceived by IITRI.

The second objective of this task is to establish the kinetics for methods which were recommended in Task 5 for engineering and economic evaluation. Kinetics were established, calculated, or estimated using the

best information available on the subject. In many cases crucial information was missing and therefore only guesses could be made. The results are reported as part of the engineering and economic evaluation of the recommended processes.

2.5 TASK 5: ENGINEERING AND ECONOMIC ANALYSIS

This task was broken down into three subtasks:

(1) Development of screening and evaluation criteria
(2) Screening of potential concepts
(3) Engineering and economic evaluation of the most promising concepts.

2.5.1 Development of Criteria

To compare and rank the many concepts that were identified and developed, it was necessary to develop quantitative criteria and a methodology to apply these criteria to these methods. Care was taken not to overly penalize or overly reward a method to the point of obscuring its true status relative to the others. In the course of this program we developed and experimented with several sets of criteria. We found that a logical approach would be to use criteria which would enable us to calculate an overall score for each process that was comparable with similar scores for other processes.

To do so we made the overall score a function of the criteria and of a weighted score for each criterion. This enabled us to express the total score mathematically in terms of the two variables as follows:

$$S = \Sigma W_i N_i$$

where S is the overall score of a process or method, W_i is the weight of criterion i and N_i is the weighted score obtained by the method corresponding to criterion i. W_i and N_i are on a scale of 0 to 10. The processes were then ranked based on their overall scores. The following example, which takes into consideration two criteria only, illustrates the method.

- Process 1 is cost effective but energy intensive
- Process 2 is expensive but conserves energy

- W(economics) = 8 out of 10
- W(energy needs) = 2 out of 10
- M_1(economics) = 7
- M_2(economics) = 3
- M_1(energy) = 1
- M_2(energy) = 8
- S_1 = (8 x 7) + (2 x 1) = 58
- S_2 = (8 x 3) + (2 x 8) = 40

Process 1 would therefore be selected over Process 2. To apply this method, we needed a procedure for determining W_i and M_i. The weighting factors were determined based on experience and engineering judgment, taking into account the government's interest through extensive discussions with the program management staff at USATHAMA.

The criteria were broken into three categories:

- Basic chemistry
- Basic process
- Process performance.

Minimum required total scores for each of the first two catagories were also established. A process was rejected if it did not meet or exceed these minimums. This procedure succeeded in filtering out processes which suffered from serious deficiencies in certain basic areas, even though high scores in other areas would have obscured the deficiencies. The criteria that were developed, the weight assigned to each criterion, and the minimum passing score for each category of criterion are given in Table 9. If a process achieved a score near or slightly below the minimum acceptable score, a qualitative re-evaluation was performed before rejection from further consideration. All evaluations were done and approved by a committee containing senior engineers and chemists in addition to the program manager at IITRI.

2.5.2 Screening of Potential Concepts

All the methods identified from the literature search and industrial survey and developed in-house were screened using the criteria and methodology described in the previous section. The screening of water hydrolysis of G3 is shown in Table 10 as an example. Results of the screening of all the methods

TABLE 9. EVALUATION CRITERIA, THEIR WEIGHTS, CATEGORIES, AND CORRESPONDING MINIMUM ACCEPTABLE SCORES

Basic Chemistry Criteria	Weight of Criterion	Minimum Acceptable Total Score at Point Indicated
Extent of reaction, can it achieve the specified effluent concentration above (10) or with added processing (8)	10	80
Rate of reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	160 (for 1 and 2)
Conditions and practicality of reactions Temperature + Pressure Room (8) 150°C (5) 300°C (2) Corrosion (2)	10	
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Extrapolated from lab data at other conditions (4)	10	
Can handle impure agents Known (10) Expected (5)	10	
Products are nontoxic	5	
Availability of reagents in large quantities	8	
Ability to handle whole munitions Known (10) Likely (6)	10	450 (for 1 through 8)
Probability that military or industry will use products	10	
Flexibility of the process equipment to handle all agents 3 agents (10) 2 agents (6) 1 agent (3)	10	
Environmental impact of waste products	10	
Safety of operating conditions 10 - intrinsic 5 - with special engr.	10	
Overall economics Capital - 5 Operation - 5	10	

TABLE 9. EVALUATION CRITERIA, THEIR WEIGHTS, CATEGORIES, AND CORRESPONDING MINIMUM ACCEPTABLE SCORES (continued)

Basic Chemistry Criteria	Weight of Criterion	Minimum Acceptable Total Score at Point Indicated
Probability of success, state of development, and ability to meet project schedule	10	1000 (for 1 through 14)
Performance of the process		
Reliability, availability, maintainability	10	
Automation capabilities and need for human interaction	7	
Layaway capability	8	
Turndown capability	7	
Site utility requirement	6	
Transportability of process	3	

TABLE 10. SCREENING OF WATER HYDROLYSIS OF GB [illegible]

	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Basic Chemistry Criteria				
Extent of reaction, can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- GB completely miscible in water. - Kinetic info extrapolated from 0-30°C, it suggests that complete destruction can be achieved in less than 1 sec.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/190	- Faster and more complete destruction is expected when distilling on some of the products, i.e., HF, alcohols - Total 190>160 = continue
Conditions and practicality of reactions Temperature • Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	5	50	- 150°C - HF highly corrosive
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated form lab data at other conditions (4)	10	4	40	- Extrapolated from lab data in the range 0-30°C
Can handle impure agents Known (10) Expected (5)	10	5	50	- Presence of impurities is not a major problem.
Products are nontoxic	5	10	50	- Major products MPA, HF, alcohol present no serious toxicity problems.
Availability of reagents in large quantities	8	10	80	- Water is available, moderate amounts needed
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot handle intact shells - Hydrolysis is normally designated to pump liquids and not solids. Variations to wash off the metal and decontaminating are possible
		Total 460 > 450		
Basic Process and Implementation Criteria				
Probability that military or industry will use products	10	10	100	- MPA may be used to produce binary munition compounds - HF may be used on industry
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Hydrolysis can be used with all three agents
Environmental impact of waste products	10	9	90	- All products can be used in industry and and the military. No substantial amounts for disposal.

TABLE 10. SCREENING OF WATER HYDROLYSIS OF GB (continued)

	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Safety of operating conditions 10 - intrinsic 5 - with special engr.	10	5	50	- Special designs may be needed to accommodate 150°C and 100 psi though not severe.
Overall economics Capital - 5 Operation - 5	10	9	90	- Liquid phase RX's. Small commercially available unit operations. However, hastelloy may be needed because HF is corrosive.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Not labor nor energy intensive and no expensive reagents or R&D needed - Chemistry is well known - Simple design - No hazardous byproducts to complicate design by introducing special treatment and disposal methods
Performance of the Process				
Reliability, availability, maintainability	10	7	70	- Commercially proven equipment - HF and impurities may necessitate more maintenance
Automation capabilities and need for human interaction	7	8	56	- T&P sensors - Override controls and auto shut-off - Automatic feed - Little man-power
Performance of the Process Criteria				
Layaway capability	8	10	80	- The equipment can be easily detoxified by circulating a caustic solution through it. It can then be drained and washed with water and dried and mothballed in a nitrogen environment. Before restarting, the nitrogen may be bubbled through a caustic solution or incinerated to guard against possible contamination.
Turndown capability	7	10	70	- Can be turned down to partial loads by controlling flow rates. - Heating may be automatically adjusted.
Site utility equipment	6	7	42	- Heating fuel and water may have to be transported to some of the sites.
Transportability of process	3	5	15	- Process is simple--made up of pumps and heaters, and column may be easily transportable by rail. This can be further facilitated by designing it in modular form.
		TOTAL = 843		
		GRAND TOTAL = 460 + 843 = 1303		

is summarized in Table 11. Details of the screening of all of the methods are reported in Appendix B.

The results in Table 11 revealed that:

(1) The difference between the total scores of many methods is small

(2) Methods which scored high for one or two agents did not score consistently high for the other agent(s).

To further screen the leading methods, which had a total score above about 1050 points, two more screening constraints were imposed. These are:

(1) Economics of the process. Special attention was paid to processes that could use the same equipment to treat all three agents. This is because the economics of one plant are most likely to be more favorable than having two or three plants.

(2) Ultimate fate of the products. Processes which produced wastes that need extensive treatment before final disposal were considered less favorable than those which produced environmentally benign wastes. More favorable treatment was given to those that produce products with high market and/or military value, such as DF.

Subjecting the leading candidates in Table 11 to these two constraints, the following candidate methods were selected for engineering and economic evaluation:

(1) Hot water hydrolysis of the three agents

(2) Pyrolysis of the three agents

(3) Anhydrous chlorinolysis of the three agents. In the case of GB this process follows a controlled pyrolysis step.

(4) Alkaline hypochlorination of GB and acid chlorinolysis of VX and H in an aqueous medium.

These four methods were analyzed and the results are presented in the following sections.

2.5.3 Engineering and Economic Evaluation of Recommended Methods

Before performing engineering and economic analyses of the recommended processes, two items pertaining to chemical methods in general were addressed:

(1) Interface of the chemical methods with possible munition disassembly techniques

(2) Preparation of the agent feed for chemical processing.

TABLE 11. SUMMARY OF SCREENING RESULTS

Method/Process	Total Score When Applied To GB	VX	H
• Hydrolysis			
Caustic Hydrolysis	1027	956	1072
Acid Catalyzed Hydrolysis	1164	*	1204
Liquid Water Hydrolysis	1303	1153	1233
Steam Hydrolysis	1200	1064	1170
Super Critical Water Hydrolysis	*	*	*
• Pyrolysis			
Conventionnal Pyrolysis	1220	1120	970
Pyrolysis using Microwaves	1085	1077	947
Pyrolysis using RF Heating	1105	1015	1015
• Direct Fluorination			
Using PF_5, SbF_3	*	NA	NA
Using HF	*	*	NA
Using Benzalfluoride	*	NA	NA
• Reactions with Chlorine-containing Compounds			
Reaction with Chlorine	*	1221	1127
Reaction with Phosgene	1062	*	NA
Reaction with PCl_3, PCl_5	*	NA	NA
Reaction with Hypolchlorites (alkaline conditions)	1181	*	*
Reaction with Thionyl Chloride	*	NA	NA
Anhydrous Chlorinolysis in Organic Solvents	1295	1305	1255
• Oxidation Reactions Excluding Incineration			
Wet Air Oxidation	1005	965	*
Reactions with H_2O_2	*	*	NA
Reactions with O_3 in Presence of UV	1010	1010	1010
• Other Methods			
Baking with Soda Ash	*	NA	NA
Reactions with Hydrogen	*	*	*
Reactions with Hydrides	*	*	*
Reactions with DS-2	*	*	*
Reactions with CD-1	*	*	*
Reactions with Sodium Sulfites	NA	NA	1169
Use of Reactive and Sorbent Resins	*	*	*
Reactions with Sodium Metal	NA	NA	*
Use of Na Pen Reagents	1098	1118	1118
Electrochemical Methods	*	*	*

TABLE 11. SUMMARY OF SCREENING RESULTS (continued)

Method/Process	Total Score When Applied To GB	VX	H
Radiolysis Using High Energy Electrons	1076	1076	1076
Direct Interaction of Microwaves with Agent Molecules	998	998	998
Photochemical Reactions--Lasers	*	*	*
Photolysis	1094	1094	1094
• Hybrid Methods			
- Controlled Pyrolysis Followed by Reaction with			
PCl_5	102R	NA	NA
$COCl_2$	104R	NA	NA
$SOCl_2$	101R	NA	NA
- Conversion of Agents to Hazardous Waste Followed by Centralized Treatment and Disposal. (This method will be evaluated separately because of its saving potential without using the criteria)			

* Rejected because of inability to meet certain minimum acceptable scores.
NA This process is not applicable to this agent.

2.5.3.1 Interface with Munition Disassembly

Even though it was beyond the scope of our contract to look at munition disassembly techniques, economic and engineering analyses could not be completely divorced from the munition disassembly method which will be adopted. We therefore examined three such methods to evaluate the impact of each on the chemical processes. These methods are:

- Punching of the agent chamber of the munition or shearing the chamber without shearing the burster chamber, and draining of the agent in a collection pot. Alternatively, removing the booster and booster well and sucking out the agent.
- Cryogenic crushing followed by remelting of the agent.
- Shearing of the munition into several sections.

Each of these methods has its own characteristics that affect the chemical processes. These are discussed below.

2.5.3.1.1 Punching or Shearing of the Agent Chamber and Draining of Agent

This method has the advantage of not contaminating the agent with explosives and propellants in case the munition is not deburstered before dismantling. If shearing is used, it would have to be done in such a way that the shearing mechanism travels only far enough to shear the outer chamber and not the inner burster chamber. If it is deburstered, then cutting through the burster well or removing it does not add any problems. For burstered munition, the punching may be done through the outer skin without reaching the well.

Metal fines due to the punching or shearing process will be collected with the agent. In the case of mustard, a substantial portion of the agent (up to 60 percent in some cases) may be in the thickened form and may not be easily drainable. Thus considerable contamination of the shell will remain.

If this method of disassembly is selected by the Army, then the interface that we envision with chemical processes will consist of the following:

(1) Drain as much of the agent as possible in a collection pot.

(2) Wash the inside and outside of the agent chamber with a suitable solvent and drain in the same collection pot. Use DMSO or acetone. The washing should be done in a counterflow manner to minimize the amount of solvent

required by the overall process. Drain the used solvent into the same collection pot.

(3) Wash the inside and outside of the shell with solvent at conditions that do not risk an explosion in the case of the burstered munition. Drain used solvent into the same collection pot used for collecting the agent. Repeat enough times to decontaminate the shell substantially.

(4) Continuously stir collection pot and feed from it into the chemical process.

(5) Treat the decontaminated shell, which may or may not contain the explosives and/or propellants. Remove explosives by melting. Dispose of the explosives and/or propellants using conventional methods. It may be possible to ship the shell to an existing plant (such as the Hawthorne Ammunition plant in Nevada) for removal of the explosives.

(6) Transport metal parts to a smelter for processing. Special handling at the smelting site is required in such a case and modification of the smelting furnace may be necessary to further ensure that complete decontamination of the metals is achieved. Transport the metals to the smelting site in rail cars. These may require some special shipping precautions, but would not require treating this as surety material. Use an on-site furnace to incinerate the explosives and the metals.

As stated earlier, these methods protect the agent from contamination with impurities from the explosives and propellants. The agent, however, will contain thickened materials and corrosion products. The solvents will break up and solubilize the thickened material, but corrosion products and metal fragments and fines from the punching process will remain. This will have to be removed to guard against fouling of the equipment.

2.5.3.1.2 Cryogenic Crushing

If this method of munition disassembly is selected, then contamination of the agents with explosives, propellants, and metal parts is likely unless the munitions are deburstered before crushing. There are three agents and six explosives and propellants in use. This makes it very difficult to estimate the magnitude of potential contamination, since some of them are soluble to some extent in organic solvents and water. Our preliminary assessment of the interface process between chemical methods and cryogenic crushing is as follows:

(1) Warm the crushed mixture gradually to about 50°C to melt the agents without melting the explosives or the propel-

lants; 50°C is more than what is required to melt the agents. The extra heating will help the flow of the agents, especially the thickened material. Agents collected this way will carry with them some explosives and propellants. These, most likely, will be in the form of solid particles, but some will also be dissolved in the agents. This mixture will be dissolved in the solvent which will be used in the chemical process. Thus the potential for explosions is virtually nonexistent. However, contamination of the products will occur.

(2) Wash off the explosive propellants and metal mixture with solvent and add the wash liquid to the agent collection tank. This will dissolve small amounts of the explosives but is not expected to cause any serious problems in the chemical process.

(3) Continue heating the crushed mixture to 130°C to melt the explosives and the propellants. The collected melt will contain agents and thus should be decontaminated, probably by incineration.

(4) After the explosives and propellants are melted out, wash the remaining metal fragments with solvent. The wash mixture should be added to the agent collection tank and fed to the chemical process after separating the corrosion products and metal fragments.

(5) The metal pieces which are decontaminated may be transported for smelting as in the previous case. If the munitions are debursteredbefore crushing, steps pertaining to explosives will be deleted.

2.5.3.1.3 Shearing of the Munition

The ordinary method of shearing the munition will result in breakage of the burster chamber as well as the agent chamber. It will contaminate the agent with explosives, and the explosive with agents unless the munition is debursteredin advance. A procedure similar to that proposed for the cryogenic case may also be used here.

The above discussion of the three possible munition disassembly methods leads to the following conclusions relating to chemical processes.

- Separation of corrosion products and other metal pieces and fines is necessary to prevent their buildup in the system.
- Contamination of the agents with explosives and propellants is not a serious operation problem but could affect the purity and marketability of final products. Debursteringof the munition before dismantling simplifies the operation considerably.

- The interface between chemical processes and the munition disassembly process is feasible.
- Chemical processes can be viewed as methods for treating the whole munition except for the destruction of the explosives and the propellants.

2.5.3.2 Feed Preparation

Agents such as GB, VX, and H are generally contaminated with suspended solids. These are generally products of corrosion of the metal containers in which the agents are stored, or chemicals that are added to the agents to modify their properties such as corrosivity and stability, or products of polymerization of the agents themselves. They may also include metal fines and fragments that may have been generated during munition disassembly. The objective of separating solids from the feed is to guard against clogging or plugging of the chemical demilitarization process equipment. Several possible separation techniques were evaluated including centrifugation, pressure filtration, vacuum filtration, and settling.

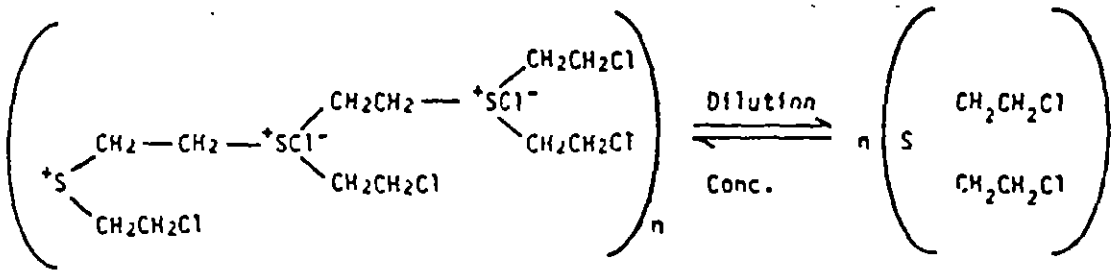
Very little information has been published on the nature or magnitude of these solids. A thorough analysis of a large number of samples from different storage containers was conducted at CAMDS[1] in March 1977. Chemical analyses of the agent samples were performed only after separating the solids either by centrifugation or by filtration, and the results are reported in enclosure 2 of the demilitarization plan operation of CAMDS in March 1977. Hence, no information was collected on the nature of the solids. However, it was noted in that report that the suspended solids content of the samples was relatively insignificant for samples of agents GB, VX, and HT. Samples of the H agent showed relatively high solids content in the drained liquid. (Two samples of the GB agent also showed high solids content).

The suspended solids present in the H agent are probably polysulfides formed by the polymerization of the agent. The polymerization reaction may have been initiated by metal oxides or hydroxides formed by the corrosion of the containers. Magnesium hydroxide was used as the nucleating agent for polymerization of mustard agent in a study by Thiokol Corporation.[17] Solids present in other agents are probably due to corrosion and erosion of the containers, which are made of either iron or aluminum. Analysis of the agent samples conducted during the CAMDS statistically significant sampling program[1] showed relatively high concentrations of iron and aluminum in the agent

samples. The aluminum content was up to 2600 ppm even after the suspended solids were separated from the GB samples. The solubility of aluminum oxides or hydroxides is extremely low even in highly alkaline solutions and therefore these solids may deposit in the process equipment and affect the demilitarization process.

The CAMDS report also showed[1] that there were large concentrations of solids with agent H during its draining operation. These solids are probably a mixture of polysulfides that are formed either during the storage or synthesis of H and contain some multimers of the agent. Vrieson[18] reported that polysulfides are in a latex form. The multimers can be redissolved in a solvent by diluting the agent. Draining operations at CAMDS were facilitated by adding a solvent.[18]

Adding a solvent can result in the formation of monomers according to the following reaction:



This will reduce the gel-like properties of the agent and make it flow easier. The addition of a solvent may also prevent coagulation of the polysulfide particles during their flow through the furnace tubes and distillation column of the hydrolysis process. Large particles of polysulfides may cause a problem by settling in the process and therefore should also be removed along with the corrosion and erosion products.

Several processes are available for separating large particles (coarser than 0.5 mm in diameter) from liquids. Conventional processes, however, such as centrifugation, pressure filtration, and vacuum filtration are difficult to use with agents because they require extensive human interaction, produce large quantities of side streams with low solids concentration, and contaminate the air stream blown across the filters. In their studies on GB-DF conversion studies, Curran et al. (Battelle)[18a] proposed distillation as a means of separating liquid agents in vapor form from the solids. Distilla-

tion, however, is an energy intensive process and thus costly. Our analysis indicates that it would be possible to separate solids larger than 0.5 mm, which could affect the process equipment, simply by using a properly designed settling chamber. This is inexpensive and easy to interface with the other process equipment.

A settling chamber is simply a large diameter vessel that can be incorporated in the liquid flow stream. The vessel is designed in such a way that the linear velocity of the fluid is lower than the sedimentation velocity of the particles that are to be separated. The performance of the settling chamber depends on the size of the particles, their density, and the properties of the fluid. Since the purpose of the separation process is only to protect the process equipment from fast settling particles, the settling chamber can be designed to separate all the particles coarser than a desired size.

Among the three agents that need to be treated by the same demilitarization equipment, agent VX has the highest viscosity, about 12 cp.[19] The settling chamber must therefore be designed to separate particles from this agent. Separation will be better with other agents since they have lower viscosities.

As described in the previous section, the agents are mixed with solvents. More solvents can be added if required by the chemical process. The viscosity of the mixture will depend on the proportion of the various constituents. Increased dilution of the agent will reduce the viscosity of the mixture and increase its flow rate. For a given size settling chamber, increase in flow rate increases the linear velocity of the fluid in the chamber which increases the size of particles that can be separated. This is partly offset by the reduced viscosity of the mixture. Particle cut-off size, defined as the largest size particle that can be separated under a given set of conditions, is shown in Figure 1 as a function of the diameter of the sedimentation chamber and the flow rate of the mixture. A total flow rate range of 2000 to 6000 lb/hr is shown. It is adequate for a 1000 lb/hr flow rate of agents and 1000-5000 lb of additional reagents. Details of the calculations are shown in Appendix B.

Figure 2 illustrates the flow diagram of the separation process. The agent mixture which is collected in the collection tank is mixed with the

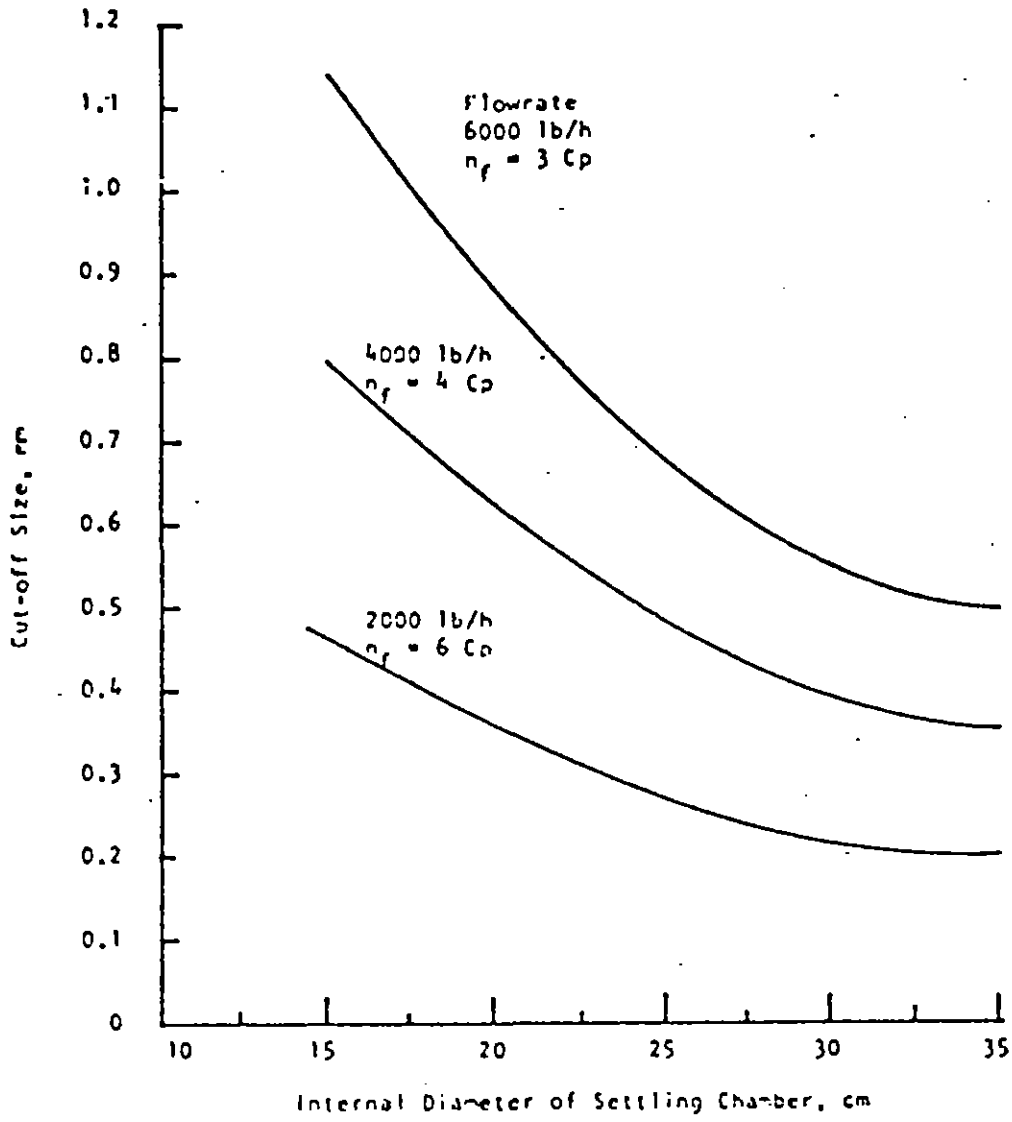


Figure 1. Cut-off particle size as a function of the diameter of the settling chamber.

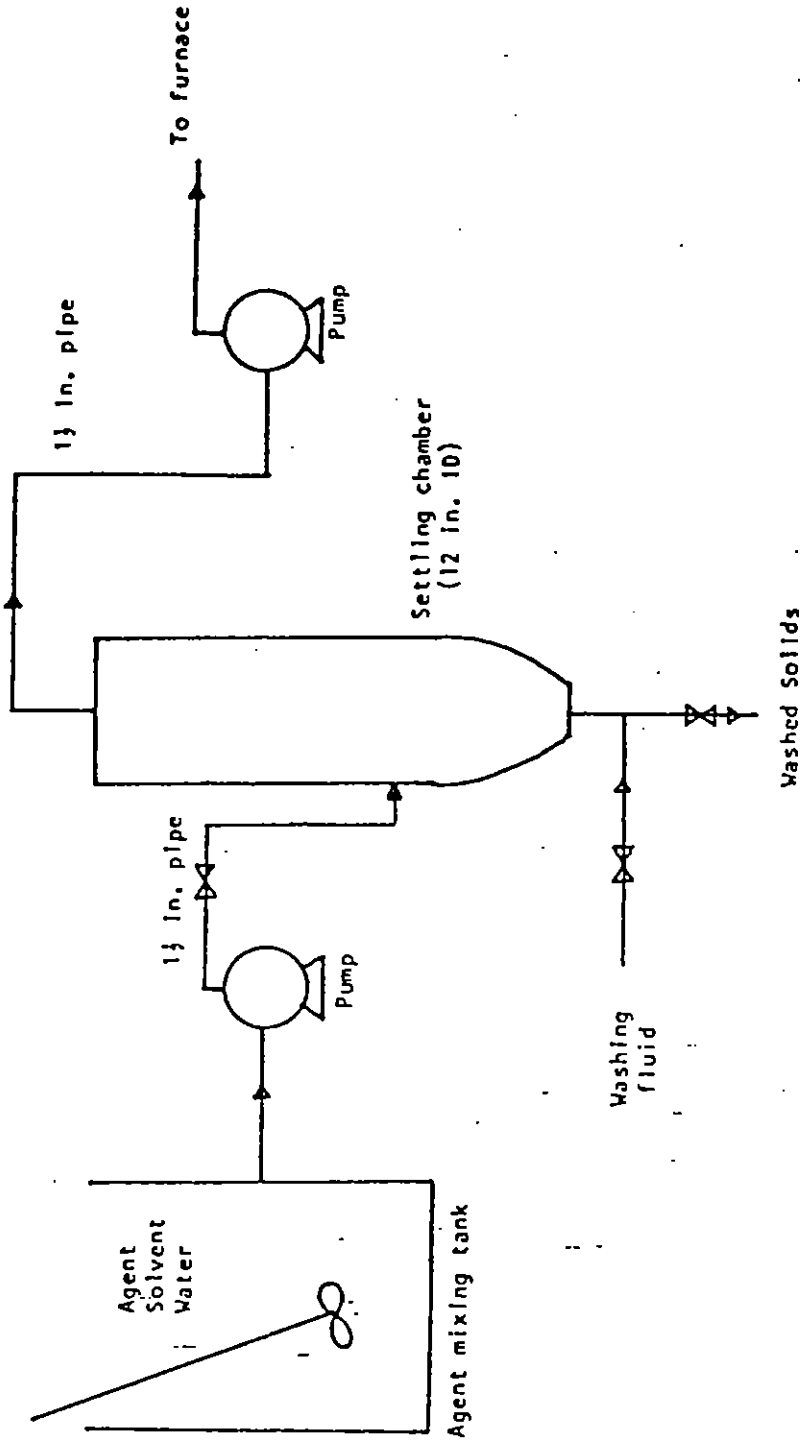


Figure 2. Schematic diagram of solids separation equipment.

required solvent and then pumped through the settling chamber, which is about 12 in. in diameter. This diameter will trap particles above about 0.5 mm in diameter. Coarse particles settle into the bottom of the chamber, whereas the agent mixture containing a small quantity of finely dispersed particles is collected from the top of the sedimentation chamber. The solids collect in the bottom of the chamber. Provisions will be made to wash the solids periodically with solvent to reduce the concentration of the agents to an acceptable level for further processing without having to shut down the system. Washed solids are dumped into a separate tank filled with caustic and stored for incineration and disposal. The incinerator which will be used for incinerating the explosives can be used to incinerate the washed solids.

The above information on interface with disassembly methods and feed preparation was incorporated into the conceptual design and evaluation of the four recommended methods discussed below.

2.5.4 Engineering and Economic Evaluation of Hot Water Hydrolysis

This section presents an engineering and economic evaluation of water hydrolysis for each of the three agents. In each case, the pertinent process flow diagram, material and energy balances, value and disposal of final products, economic analysis, and comparison with the RSD baseline are discussed. The same procedure is followed in analyzing the other three methods.

2.5.4.1 Kinetics

Attempts were made to establish the kinetics of the hydrolysis process in order to calculate the data necessary for estimating the sizes of the major equipment as well as to assess the feasibility of having a continuous process. We gathered the relevant data in the literature and discussed the subject with our consultant, Dr. Joseph Epstein. The results for the three agents are as follows:

2.5.4.1.1 Kinetics of Water Hydrolysis of GB

In the case of GB, the estimated dependence of the hydrolysis rate on pH is shown in Figure 3. The rate increases as the pH is lowered from 4.0. It also increases as the pH increases above 6.5. Starting with a solution of GB in tap water, the initial pH should be equal to or less than 7. As hydrolysis

proceeds, the pH drops rapidly to the acid range because of the production of HF and isopropyl methyl phosphonic acid.

Data on the effect of temperature on the hydrolysis rate catalyzed by hydrogen ions are not available. From temperature data on other organic esters, which show pH rate dependencies similar to those of GB,[20,21] the activation energy for the acid-catalyzed hydrolysis of GB should be approximately 14 kcal/mole. Using this value and the data on the hydrolysis rate of GB at 30°C, which is shown in Figure 3 for acid pH levels of 0-4, it is possible to calculate the rate of hydrolysis at 150°C. For instance, 1 lb GB in 1 gal water, with a few milliliters of concentrated HCl to lower the pH to about 3, will undergo 90 percent hydrolysis of GB in 1 second at 150°C. Increasing the acidity and/or increasing the concentration of GB will increase the rate of the reaction. This implies that the required residence time to reduce the concentration of a one-molar solution of GB to the parts-per-billion level can be measured in seconds. The rate is therefore expected to be very rapid and not process limiting.

2.5.4.1.2 Kinetics of Water Hydrolysis of VX

Data are available on the hydrolysis of VX at 25°C and various pH levels,[22] but are fragmentary at different temperatures and different pH levels. Because of the lack of adequate data we assumed that the dependence of the rate on temperature and pH is similar to that of GB, for which data in the alkaline pH range are available. Based on this assumption and the above-mentioned data, the half-life equation was calculated to be:

$$\ln (t_{1/2}) = 11578\ T^{-1} - 2.2917\ pH - 15.924$$

The hydrolysis of VX is further complicated by the fact that the decomposition process produces a potentially harmful product. To minimize the production of this product and to attain a rapid rate of reaction, we determined that a pH of 12 is necessary at 150°C. This pH can be reached by adding ethanolamine, which will also increase the solubility of VX. Our calculations show that at the indicated pH and temperature, the half-life of VX will be less than 5×10^{-4} seconds, and the product mix will contain no more than 2 percent of the potentially harmful material.

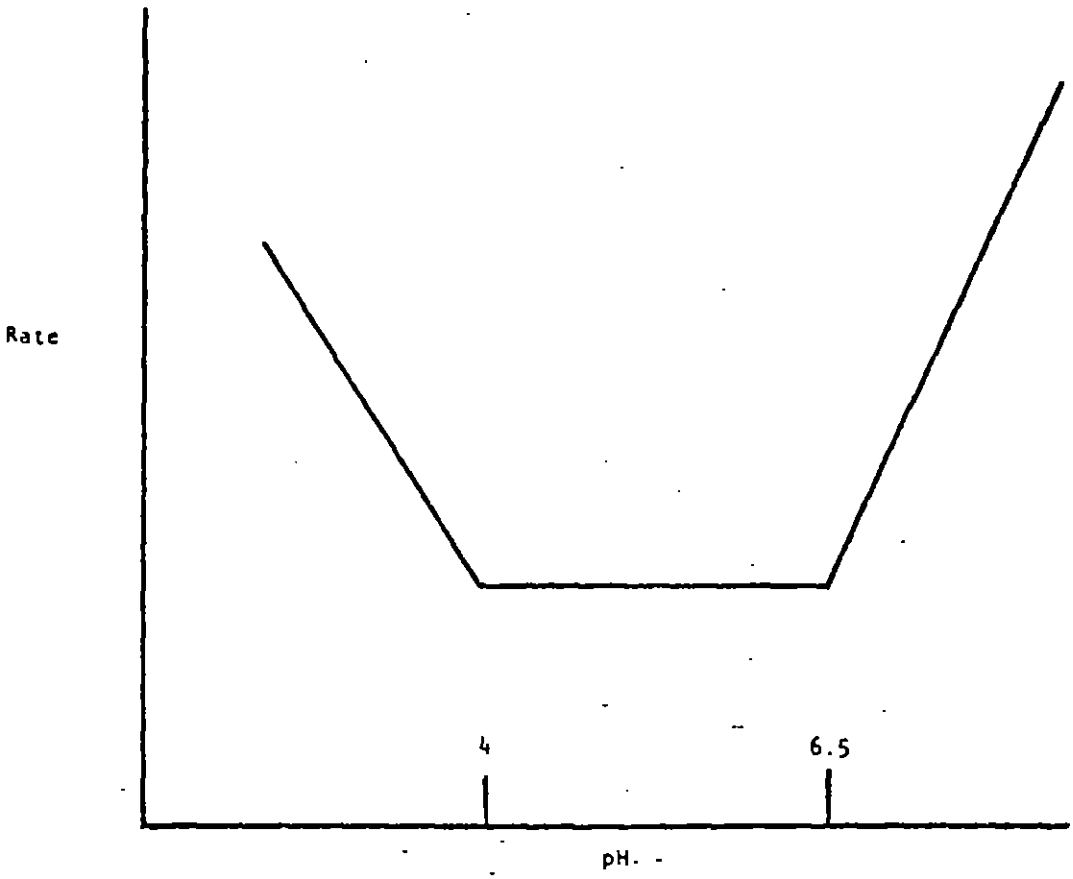


Figure 3. Dependence of hydrolysis rate of GB on pH.

2.5.4.1.3 Kinetics of Water Hydrolysis of H

In the case of mustard, the literature value for the rate constant k is 0.098 at 25°C in acetone solution.[23] We made the following assumptions to calculate a k-value of 567.7 at 150°C:

- Rate constant doubles with every 10°C rise in temperature
- First-order reaction: $\ln (1-X_a) = kT$
- Rate is virtually independent of pH.

The corresponding required residence time to reduce the concentration of a one-molar solution of H to the parts-per-billion level is about 0.03 seconds, thus kinetics are not expected to be process limiting. This rate applies in the presence of acetone to solubilize H. Without a solvent such as acetone, the solubility of H in water, which is extremely low, may become the limiting step. Other solvents may then be preferable to acetone at high temperatures and thus should be made part of the laboratory testing program.

2.5.4.2 Process Description

Figure 4 is a simplified schematic diagram of the proposed process. A mixture is made of the agent that has been removed from the munition that may be mixed with water, solvents, and traces of explosives and propellants. If needed, more solvent and water is added to the mixture, which then goes through the settling chamber to separate any solid particles larger than 0.5 mm in size, as shown earlier in Figure 2. The mixture is heated by passing through a gas-fired furnace or by heat exchange with steam. The flow velocity through most of the tubes (25 in. ID) will be about 15 ft/sec.

At this rate the flow will be turbulent and considerable mixing will occur within the pipes. To ensure perfect mixing, a static mixer must be added before the distillation column. The cost of the mixer is insignificant compared to the total cost of the system and therefore it is wise to keep it at this stage of the analysis. As the mixture exits the mixer it would have spent several seconds at the hydrolysis conditions and thus must be degraded to the parts-per-billion level, as suggested by the kinetics calculations for all of the three agents. The detoxified mixture is then fed to distillation columns to separate the products. The separation processes are intended to:

(1) Remove one or more of the products to drive the reaction to completion and to prevent reformation of the agent.

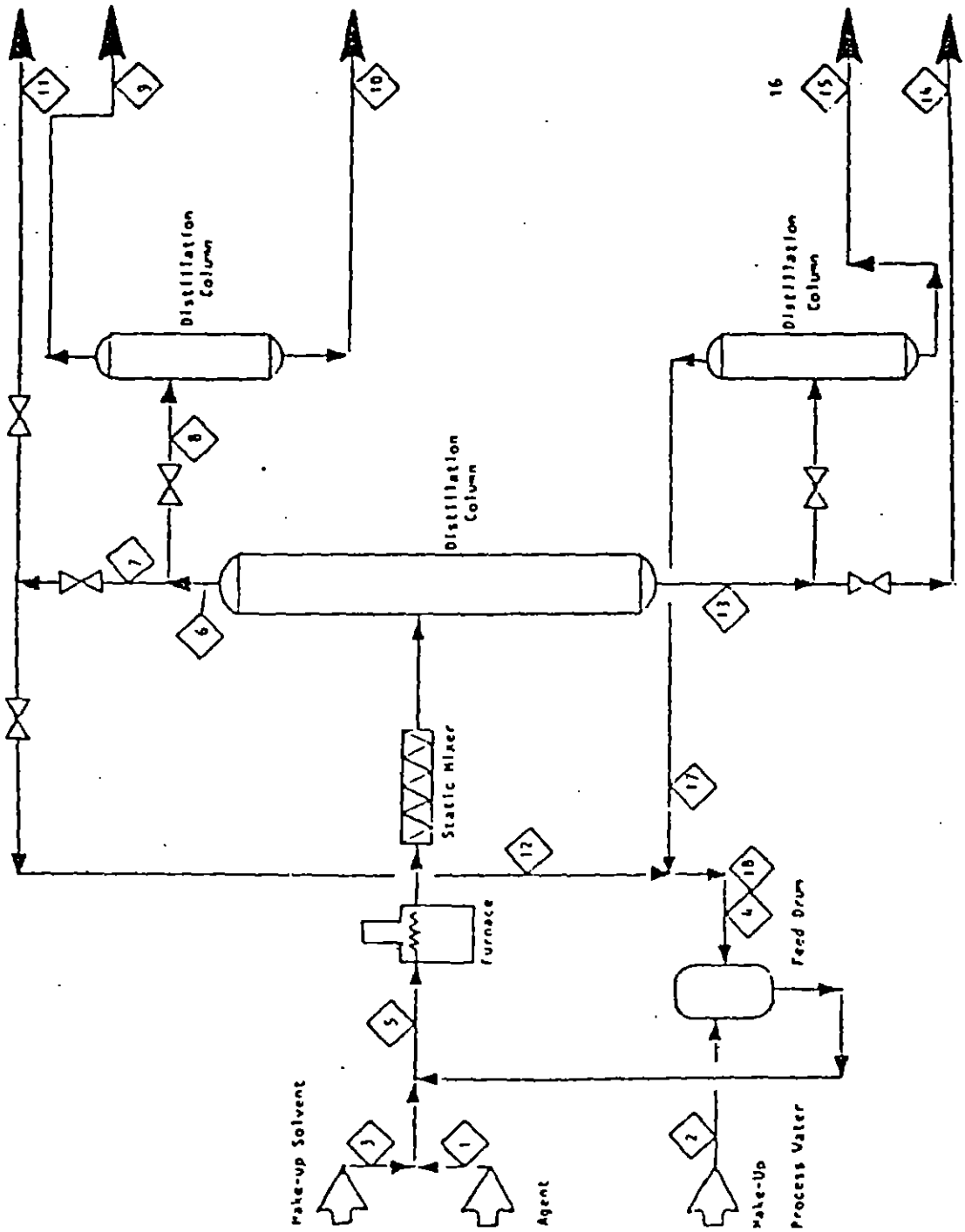


Figure 4. Simplified schematic diagram of the hydrolysis process.

(2) Recover useful products in pure states.

(3) Recycle as much of the water and solvent as possible to reduce operating cost and to reduce the amount of waste products that require disposal.

Figure 5 is a more detailed process flow diagram which contains all the equipment required for the hydrolysis of the three agents. Not all of the equipment is required in each case. GB hydrolysis makes use of all of the system, VX hydrolysis does not need distillation columns DC-102 and DC-103, and H hydrolysis does not need distillation column DC-102. The configurations of Figure 5 that are pertinent to the hydrolysis of each of the three agents are discussed below.

2.5.4.2.1 Hydrolysis of GB

- GB + H_2O → HF + iPrOH + MPA.
- GB is soluble in water and thus no solvent is required.
- Hydrolysis will be carried out at 150°C and 150 psig.
- iPrOH and HF are saleable products. MP may be used to produce DF. Thus there are no waste products.

Process Description. A mixture of water and GB, which may contain traces of impurities (explosives, propellants) and some corrosion products and metal fines, will pass through the settling chamber, the furnace, and the static mixer. The mixture at this stage will consist primarily of water, hydrogen fluoride (HF), isopropyl alcohol (iPrOH), and methyl phosphonic acid (MPA). Since each of these compounds is a desired product, complete separation of the mixture is warranted. A distillation column can be designed to separate the four compounds.

Economics, size, and ease of operation, however, favor a three-step separation as shown in Figure 4. Three columns are used for this purpose. The first (DC-101) is a bubble cap column, the other two (DC-102, DC-103) are packed columns. In the first column (DC-101), azeotropes of isopropyl alcohol and HF are distilled off at the top while MPA and water are collected at the bottom. The mixture from the top of the column is fed to column DC-102 to separate the HF azeotrope from the isopropyl alcohol azeotrope. When hydrolyzing GB, block valves BV-102 and BV-103 in Figure 5 must be kept closed at all times.

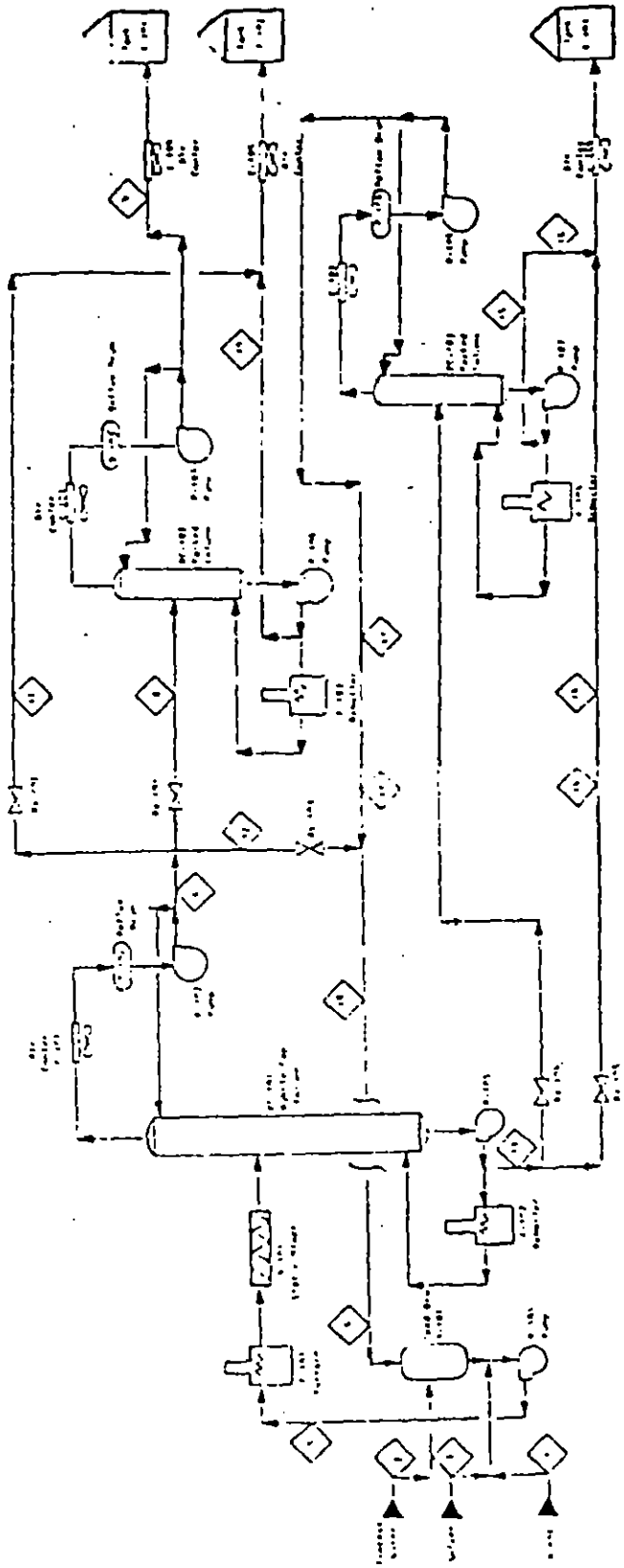


Figure 5. Detailed process diagram of the water hydrolysis process.

In the second column (DC-102), isopropyl alcohol azeotrope is collected at the top and HF azeotrope at the bottom. Each of the two products is stored in tanks sized for a 15-day supply before shipping to the end user. The process will be more complicated if a tertiary azeotrope (HF, isopropyl alcohol, water) is formed. Different separation techniques will have to be devised.

The bottoms from the first column (MPA and water) are sent to the third column (DC-103). The excess water is boiled off and returned to the hydrolysis process and MPA is collected in a 15-day storage tank until being shipped to the end user.

2.5.4.2.2 Hydrolysis of VX

- VX + H_2O → Water-soluble compounds
- VX is not very soluble in water; ethanolamine will have to be added to solubilize VX.
- Hydrolysis will be carried out at 150°C and 150 psia.
- Products require further processing and disposal.

Process Description. The system depicted in Figure 5 will also be used for the hydrolysis of VX. The agent/solvent/water mixture which is collected in the agent collection tank will pass through the settling chamber, the furnace, and the static mixer as in GB hydrolysis. Kinetics suggest that the material leaving the mixer will contain only parts-per-billion concentrations of agent.

The primary products at this stage are two water-soluble compounds that have no market value and must be disposed of properly. The product mix also contains excess water and ethanolamine. The product mix is therefore fed to the first column (DC-101) to recover the excess water and the ethanolamine and return them to the system. This also reduces the volume of the waste products. Since no further separation is needed, block valves BV-101, BV-103, and BV-104 are kept closed during the hydrolysis of VX. The compounds which still contain enough water to keep them in solution are pumped into a 15-day storage tank for disposal. This is the same tank which will be used for storing HF in the case of GB hydrolysis.

The compounds produced from the hydrolysis process have no market value and will be disposed of by incineration. Three alternatives were considered for this purpose:

- Contract with a waste management company to incinerate it.
- Transport to a centrally located incinerator owned by the government.
- Construct and operate an incinerator on site.

2.5.4.2.3 Hydrolysis of Mustard

- H + H_2O + HCl + Thiodiglycol
- H is insoluble in water. DMSO or acetone will be used as a solvent.
- Hydrolysis will be carried out at 150°C and 150 psig.

Process Description. The basic system shown in Figure 5 will also be used for the hydrolysis of H. DMSO or acetone is added to solubilize the mustard and unthicken the jellied material. The mixture from the agent collection tank is pumped through the settling chamber. Kinetic analysis suggests that almost complete detoxification will occur in the process and only parts-per-billion levels of agent will remain. The products are primarily HCl and thiodiglycol. HCl and H_2O may be distilled off and recovered as an azeotrope from the top of column DC-101. The bottoms, which contain thiodiglycol, excess water, and small amounts of the solvents can be fed to the third column (DC-103) to recover the water and the solvent and thiodiglycol can be collected. The HCl and thiodiglycol are stored in 15-day tanks. Block valves BV-101 and BV-103 are closed during the hydrolysis process.

2.5.4.3 Material and Energy Balances

Material and energy analysis were performed on the three configurations of Figure 5 as they apply to the hydrolysis of 1000 lb of agent per hour for each of the three agents. The results from the material balance analysis are summarized in Tables 12, 13, and 14 for GB, VX, and H respectively.

The energy balance analysis was restricted to the estimating the duty of the furnaces and the coolers in the process diagram in order to determine their relative sizes and costs. The results are summarized in Table 15. Air coolers are used instead of water coolers because many of the sites are located in desert-like areas where water conservation is important, and any leakage would create a large volume of contaminated water.

TABLE 12. GB-HYDROLYSIS OVERALL MATERIAL BALANCE CALCULATIONS AT STEADY STATE IN LB/HR
(Basis - 1000 lb/hr GB)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
GB	1000	0	0	0	1000	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2O	0	644	0	6494	7138	318	0	318	60	258	0	0	6563	0	69	69	6494	6494
MPA	0	0	0	0	0		0	0	0	0	0	0	685	0	685	685	0	0
HF	0	0	0	0	0	143	0	143	0	143	0	0	0	0	0	0	0	0
IPrOH	0	0	0	0	0	429	0	429	429	0	0	0	0	0	0	0	0	0
TOTAL	1000	644	0	6494	8318	890	0	890	489	401	0	0	7248	0	754	754	6494	6494

TABLE 13. VX-HYDROLYSIS OVERALL MATERIAL BALANCE CALCULATIONS AT STEADY STATE IN LB/HR
(Basis - 1000 lb/hr VX)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
VX	1000	0	0	0	1000	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2O	0	682	0	2477	3159	2477	2477	0	0	0	0	2477	619	619	0	0	0	2477
Ethanol Amine	0	0	70	280	350	280	280	0	0	0	0	280	70	70	0	0	0	280
Salt 1	0	0	0	0	0	0	0	0	0	0	0	0	957	957	0	0	0	0
Salt 2	0	0	0	0	0	0	0	0	0	0	0	0	106	106	0	0	0	0
TOTAL	1000	682	70	2807	4509	2757	2757	0	0	0	0	2757	1752	1752	0	0	0	2757

TABLE 14. H-HYDROLYSIS OVERALL MATERIAL BALANCE CALCULATIONS AT STEADY STATE IN LB/HR
(Basis - 1000 lb/hr H)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	1000	0	0	0	1000	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2O	0	3148	0	2510	5658	2467	2467	0	0	0	2647	0	2780	0	270	270	2510	2510
DMSO (Dimethyl Sulfoxide)	0	0	94	535	629	0	0	0	0	0	0	0	629	0	94	94	535	535
HCl	0	0	0	0	0	459	459	0	0	0	459	0	0	0	0	0	0	0
Thiodiglycol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	768	768	0	0
TOTAL	1000	3148	94	3045	7287	3101	3101	0	0	0	3101	0	4186	0	1141	1141	3045	3045

TABLE 15. SUMMARY OF DUTY OF HEATERS AND COOLERS WITH EACH OF THE THREE AGENTS

Item	Btu/hr			
	GB	VX	H	Design
Furnace F-101	220,000	500,000	806,000	970,000
Furnace F-102	1,050,000	3,000,000	3,350,000	4,020,000
Furnace F-103	230,000	--	--	275,000
Furnace F-104	8,000,000	--	3,730,000	9,600,000
Air Cooler C-101	980,000	2,850,000	3,200,000	3,800,000
Air Cooler C-102	7,590,000	--	3,550,000	9,100,000
Air Cooler C-103	220,000	--	--	255,000
Air Cooler C-104	78,000	--	--	93,000
Air Cooler C-105	65,000	--	500,000	604,000
Air Cooler C-106	73,000	170,000	110,000	204,000

2.5.4.4 Design Criteria of the Hydrolysis System

The following criteria were adopted for Figure 5 so it could serve as a basis for performing an economic evaluation that could be compared with the RAD baseline:

- System should be adaptable to all three agents. This makes it necessary to include the largest sizes required by any of the three agents.
- Process temperature: 150°C; pressure: 150 psia.
- Agent concentration in feed to process corresponds to 1 molar in water for GB, 1 molar in solution (~1.1 molar in water) for VX and H.
- Residence time inside the first distillation column (DC-101) is 30 minutes; the column is operated at about 135 psig pressure.
- Design basis: 1000 lb/hr of agent.

Based on the above criteria the essential equipment was sized for economic evaluation as shown below:

Column — Many essential data for calculating actual design parameters such as volatility data of the compounds in the mixture were lacking and could only be generated experimentally, which was beyond the scope of this work. Conservative engineering judgment was therefore used to size these

	columns. A total residence time in the first column of 30 minutes was incorporated into the sizing process to guarantee the destruction of all traces of the agent.
Drums	Sizing was based on the flow rate in the inlet streams to these drums.
Coolers and Heaters	Sizing was based on the largest heat duty they encounter with any of the agents.
Pumps	Sizing was based on their largest inlet flow rate.
Tanks	Designed for 15-day storage under full-load operations.
Valves	All are block valves and are small in size, and add little to the total cost. They have to fit the sizes of the pipes on which they are installed.
Static Mixer	Manufactured by Chemineer Kenics, its cost is very small relative to the total cost of the system and its importance to the proper operation of the system is questionable. A 25 element mixer was selected.
Setting Chamber	Discussed previously in this report.

Based on the above criteria an equipment list was prepared showing the required components (Table 16).

The above discussion shows that water hydrolysis is a simple process which uses commercially available equipment. It can be used to destroy all three agents and produce useful products from GB and H. It is technically feasible with high confidence and no serious problems are anticipated. We therefore assessed its economic competitiveness.

2.5.4.5 Economic Evaluation

The economic evaluation of the hydrolysis process addressed the following items:

- Capital equipment cost
- Operating cost
  - materials
  - labor
  - others
- Cost of disposal of nonmarketable by-products
- Cost of disposal of explosives and metals
- Market value of useful products
- Comparison with the baseline.

TABLE 16. LIST OF EQUIPMENT FOR THE HYDROLYSIS PROCESS--ALL MADE OF HASTELLOY B

Item	Design Criterion	
Distillation Column		
DC-101	2 ft diameter, 20 buhhle cap trays, 18 in. between trays (40 ft total)	
DC-102	8 in. diameter, 25 ft packed zone, (35 ft total)	
DC-103	2 ft diameter, 25 ft packed zone, (35 ft total)	
Drum		
D-101	3 ft x 6 ft	(Diameter x Length)
D-102	2 ft x 4 ft	(Diameter x length)
D-103	1 ft 3 in. x 2 ft 6 in.	(Diameter x length)
D-104	2 ft 6 in. x 5 ft	(Diameter x length)
Cooler (Air)		
C-101	3.8 MMBtu/hr	
C-102	9.1 MMBtu/hr	
C-103	265 MBtu/hr	
C-104	93 MBtu/hr	
C-105	604 MBtu/hr	
C-106	204 MBtu/hr	
Heater		
F-101	1.0 MMBtu/hr	
F-102	4.0 MMBtu/hr	
F-103	275 MBtu/hr	
F-104	9.6 MBtu/hr	
Pump		
P-101	20 gpm; 3 hp	
P-102	11 gpm; 0.2 hp	
P-103	2 gpm; 0.05 hp	
P-104	20 gpm; 0.3 hp	
P-105	21 gpm; 0.3 hp	
P-106	2 gpm; 0.05 hp	
P-107	4 gpm; 0.1 hp	

TABLE 16. LIST OF EQUIPMENT (continued)

Item	Design Criterion
Tank	
T-101	30,000 gal (based on storage of products for 360 hours of operation)
T-102	140,000 gal
T-103	80,000 gal
Valve (block only) - Small	
BV-101	1/2 in. (cost included with piping)
BV-102	3/4 in. (cost included with piping)
BV-103	3/4 in. (cost included with piping)
BV-104	1 in. (cost included with piping)
BV-105	1.2 in. (cost included with piping)
Static Mixer	
K-101	25 elements

2.5.4.5.1 Capital Equipment Cost.

The installed cost of each of the components shown in Table 17 was estimated using information and techniques from the following two sources:[24,25] Modern Cost Engineering Techniques by H. Popper, McGraw Hill Book Company, 1970, and Modern Cost Engineering published by Chemical Engineering magazine, 1979. All reported costs are in 1982 dollars. The base year in these references was 1959. The 1959 prices were multiplied by 3.15 to obtain 1982 prices. This is according to the recommendation of the December 27, 1982 issue of Chemical Engineering magazine. The results are summarized in Table 17 for a plant which is designed to process 1000 lb/hr of any of the three agents.

The total installed cost of the equipment is $1,460,000. This does not include the cost of the small block valves which is part of the cost of piping. The most expensive items are distillation column DC-101, cooler C-203, heaters F-101, F-102, and F-104, and the three storage tanks T-101, T-102, and T-103. We believe that DC-101 is oversized and the actual column should be smaller and less expensive. The lack of adequate data make it necessary to assume the larger size to be on the conservative side.

TABLE 17. INSTALLED EQUIPMENT COST

Item	Installed Cost ($ 1982)
Distillation Column	
DC-101	244,000
DC-102	11,500
DC-103	39,800
Drum	
D-101	31,700
D-102	22,600
D-103	16,400
D-104	26,000
Cooler (Air)	
C-101	31,000
C-102	69,000
C-103	10,400
C-104	3,600
C-105	7,000
C-106	6,400
Heater	
F-101	56,000
F-102	147,000
F-103	20,000
F-104	248,000
Pump	
P-101	12,300
P-102	7,900
P-103	7,000
P-104	8,600
P-105	9,000
P-106	7,000
P-107	7,300
Tank	
T-101	89,000
T-102	178,000
T-103	134,000
Valve (block only, all small)	
BV-101	Included with piping
BV-102	Included with piping
BV-103	Included with piping
BV-104	Included with piping
BV-105	Included with piping
Static Mixer	5,000
Settling Chamber	5,000
Total Installed Equipment Cost	1,460,000

IIT RESEARCH INSTITUTE

The installed equipment cost is also summarized per category in Table 18. This table shows that the cost of piping is estimated to be 25 percent of the total installed cost of the equipment. This high percentage covers the need for double piping to contain leaks. The outer layer will be made of a suitable plastic material and the annulus between the two pipe layers will be monitored by purging with nitrogen and analysis of the gas. Another 25 percent of the total cost of equipment and piping covers R&D effort and final design of the plant. This is also probably on the high side. The total capital investment in 1982 dollars (equipment, piping, and design) is $2.28 million.

TABLE 18. TOTAL CAPITAL INVESTMENT 1982 BASIS
(100 lb/hr Agent)

Item	Installed Cost, $
Distillation Column	
DC-101	244,000
DC-102	11,500
DC-103	39,800
Drums	97,000
Coolers	127,000
Heaters	471,000
Pumps	60,000
Tanks	401,000
Mixer	5,000
Settling Chamber	5,000
Total Installed Cost	1,460,000
Piping (~25% of total installed cost)	365,000
Total Capital Investment (ex cont)	1,825,000
Design (25%)	456,000
Total Installed Cost of the Hydrolysis Plant	2,281,000

2.5.4.5.2 Operating Cost.

Calculation of the operating cost is somewhat complex because it involves things such as availability of the plant, amounts of agent which will be

processed per site, and labor requirements. The following assumptions were made:

(1) Plant will be designed to process 1000 lb of agent per hour.

(2) A reliability analysis was performed for the hot water hydrolysis process for neutralizing chemical agents, excluding the availability of the disassembly section. The analysis was based on the process for GB because it is the most complex, involves the most corrosive product (HF), and uses more components than the other agents. From a reliability standpoint, it is expected to be a "worst case." The following tasks have been accomplished in this effort:

- A failure modes and effects analysis was completed to identify more clearly the interrelationships between the various system components and the types of failures that can occur.
- A fault tree logic diagram was developed to clarify the logical interrelationships between the various failure modes.
- "Down times" were estimated for each failure scenario (maintainabilities).
- Failure rates were obtained for each failure scenario.

A first estimate of system availability has been computed based on the four steps above. The availability estimate was found to be 0.981.

Details of the calculation of system availability are given in Appendix C. Because of lack of information about the availability of the disassembly section, we could not calculate the overall availability of the plant. Therefore, even though the availability of the hydrolysis process is calculated to be 0.981, we used an overall availability of 0.75, a very conservative figure in this case. It could be economically justifiable to install two disassembly units in parallel to increase the overall availability of the plant. An availability of 0.75 was also adopted in evaluating all the other chemical methods discussed in this report.

(3) Each of the 10 sites contains 16,000 tons of agents in the ratio of 6:3:1-H:GB:VX. Based on 1000 lb/hr of agent, and 20 hours per day, 250 day per year operation, and assuming 0.75 availability, the duration of the project will be 0.85 years.

(4) Cost per unit of energy and water is assumed to be the same as in the baseline for electricity, fuel oil, and water.

(5) Labor requirements for the hydrolysis process are expected to be five men per shift at an average rate of $50,000 per man-year.

(6) Cost of spare parts is 6 percent of the total installed cost of the hydrolysis plant (see Table 19).

Using these assumptions, we calculated the expected total operating cost of the hydrolysis plant (summarized in Table 19).

TABLE 19. OPERATING COSTS BASED ON (1000 lb/hr Operation) HD/GB/VX RATIO 6/3/1 (0.85 Years)

Item	Consumption	Cost, $
Raw Material		
Ethanol amine	26,250 lb	33,730
Dimethyl sulfoxide	211,500 lb	164,970
Utilities		
Electricity	161,360 kWhr	8,070
Water	976,000 gallon	510
Fuel oil	228,340 gallon	274,000
Fixed Costs		
Labor: 5 men/shift, 3 shifts, $50,000		637,500
Spare parts: 6% of capital		116,370
Process-Specific		
Total Operating Costs		1,211,900

2.5.4.5.3 Cost of Disposal of By-Products

As stated earlier, the products from hydrolyzing GB and H are useful and marketable products, whereas the products from the hydrolysis of VX, water-soluble salts have no market value, and will have to be disposed of properly.

Four companies were contacted about incinerating the waste: Waste Management Company of Oak Brook, Illinois; Rollins Environmental Services of Deer Park, Texas; Stauffers Chemicals of Westport, Connecticut; and SCA of Chicago, Illinois. Based on these contacts we concluded the following:

(1) Assuming the 10 munition sites are scattered over all the United States, the average required transportation distance is 1500 miles. At 5¢/gal/100 miles, the cost of transporting the VX wastes will be $50,250, i.e.:

$$1500 \text{ miles} \times \frac{\$0.05}{\text{gallons (100 miles)}} \times 67{,}000 \text{ gallons} = \$50{,}250$$

(2) The base charge for incineration is 50¢/gal:

$$\frac{\$0.50}{\text{gallon}} \times 67{,}000 \text{ gallons} = \$33{,}500$$

(3) Normally a supplemental fuel charge is added to waste that has a heating value less than 8000 Btu/lb. We calculated the heating value of the VX wastes about 8000 Btu/lb, thus no supplemental fuel charges are required.

The heating value is calculated as follows. In the VX hydrolysis process, the overhead fraction containing excess water and recycled ethanolamine is recycled. The bottom fraction will contain some water, some ethanolamine, and the product compounds in the following proportions:

VX +	H_2O +	EA +	H_2O +	EA +	(nontoxic product compounds)
1000 lb	682 lb	70 lb	619 lb	70 lb	1063 lb

Each site has 10 percent VX or 320,000 lb. Processing at 1000 lb/hr produces 1752 lb of liquid to be disposed of each hour. Total waste would therefore be:

$$320{,}000 \text{ lb} \times \frac{1752}{1000} = 560{,}000 \text{ lb or about } 67{,}000 \text{ gal}$$

A 100-hour work week produces 175,200 lb of waste liquid; three weeks effort would complete the processing of the CW agent.

The products, which have a high organic content, have an estimated heat of combustion of 12,500 Btu/lb. The ethanolamine has a heat of combustion of 11,000 Btu/lb. The heating value of the liquid is:

$$\begin{aligned} 1063 \times 12{,}500 &= 13{,}300{,}000 \\ 70 \times 11{,}500 &= \quad 770{,}000 \\ &\overline{\qquad\qquad\quad} \\ &14{,}070{,}000 \end{aligned}$$

$$\frac{14{,}070{,}000}{1752} = 8000 \text{ Btu/lb}$$

The combustion of this liquid proceeds as follows:

$$NSPO_3C_{11}H_{27} + HOCH_2CH_2NH_2 + 23O_2 + 92N_2 \rightarrow 13CO_2 + 17H_2O + SO_2 + 1/2P_2O_5 + 93N_2$$

1063 lb 70 lb 1911 lb 982 lb 240 lb 266 lb 8500 lb

The stack gas composition is:

CO_2	1911 lb	15.2 wt%
H_2O	1601 lb	12.8 wt%
SO_2	240 lb	1.9 wt%
P_2O_5	8500 lb	68.0 wt%

The theoretical flame temperature can be calculated as follows:

CO_2 @ Cp	0.20 x 1911	= 382
H_2O @ Cp	0.45 x 1601	= 720
SO_2 @ Cp	0.20 x 240	= 48
P_2O_5 @ Cp	0.20 x 266	= 53
N_2 @ Cp	0.24 x 8500	= 2020
		3223

Available Heat: 8000 x 1752 = 14,000,000

Vaporize 1601 lb H_2O = -1,600,000

12,400,000 Btu

$$\frac{12,400,000}{3223} = 3800°F\ \Delta t$$

To summarize, VX waste material from one site could be processed in an incinerator rated at about 13,000,000 Btu per hour. It would have to be equipped with both SO_2 and P_2O_5 and NO_x scrubbing systems. Total waste to be processed is 567,000 lb.

(4) Incineration of the VX wastes has not been certified before, nor has an incinerator been equipped to serve P_2O_5, SO_2, and NO_x. The cost of modifying and certifying the incinerator is estimated to be between the $250,000 and $500,000 range. For this analysis we adopted $500,000. This charge will be shared by the 10 sites, making the average charge per site $50,000.

The above analysis leads to a total cost of incinerating the waste generated from each site of $133,750.

2.5.4.5.4 Cost of Thermal Treatment of Metals and Explosives.

Even though metals and explosives will be washed with hot water and solvents, they may still not be 100 percent agent free. Each site will produce about 19.8 million lb of metals and 1.7 million lb of explosives and propellants, as shown in Table 20. As far as the explosives are concerned, there is no viable alternative to incinerating them on site. For this analysis we will assume that the substantially decontaminated metal (washed with hot water and solvents and maybe decon solution) will be incinerated. The explosives will also be incinerated on site in a small rotary kiln or even an open hearth stationary incinerator. The estimated cost of such an incinerator is given below.

The cost of a 400-500 lb/hr kiln, installed, is estimated at $2 million. This number was derived in consultation with Mr. Val Daina of Midland Ross. The operating costs of the kiln were estimated as follows:

Labor: 3 men x 0.85 yr x $50,000/yr	= $0.128 x 10^6
Utilities (minimal), estimated	= $0.020 x 10^6
Maintenance: 6% x 0.85 yr x $2 x 10^6	= $0.102 x 10^6
Total equipment and operation costs per site	= $2.250 x 10^6

2.5.4.5.5 Total Cost.

The costs obtained in the sections above can be summarized as follows:

Hydrolysis process (equipment and operation)	$3.493 x 10^6
Cost of disposal of by-products	0.134 x 10^6
Cost of incineration of explosives (equipment and Operation)	2.250 x 10^6
Total Cost of Process Per Site	5.877 x 10^6

TABLE 20. METALS AND EXPLOSIVES ASSOCIATED WITH THE CHEMICAL MUNITIONS AT EACH SITE

No.	Munition Type	Total Metals, lb	Total Explosives, lb
80,000	115 M55 rocket		
	80,000 x 23.8	1,904,000	
	80,000 x 3.28		256,000
	19.3 M28		1,342,000
50,000	155 mm projectile		
	x 93.5	4,670,000	
	10,000 x .41 TTyl		4,100
50,000	8 in. projectile		
	x 184.5	9,220,000	
50,000	105 mm x 41.3	2,060,000	
	x 1.1 TTyl		55,000
50,000	Mortar		
	x 18.86	940,000	
	x 0.14 TTyl		7,000
	x 0.4 MG		20,000
20,000	Mine x 11.7	234,000	
	x 0.8 B		16,000
800	Bomb x 505	404,000	
200	Spray tanks		
	x 579	115,000	
200 Ton	Con x 1400	280,000	
Total		19,800,000	1,700,000

2.5.4.5.6 Value of Products

The estimated value of the products that will be produced by the hydrolysis method are summarized in Table 21.

The most likely use for MPA is by the military to convert it to DF. This can be achieved via anhydrous chlorinolysis of MPA followed by fluorination. (This method is evaluated in Section 2.5.3.5 of this report.) The MPA would have to be dried before being chlorinated, but it would still save the Army money since they would not have to buy starting materials for manufacturing DF.

TABLE 21. VALUE OF PRODUCTS DERIVED FROM THE HYDROLYSIS PROCESS

Item	Source	Quantity Per Site, lb	Value, $/lb	Total Value, $
HF-36%	GB	451,000	0.020	9,020
iPrOH-87%	GB	550,000	0.240	132,030
MPA-90%	GB	848,000	0.500*	381,600
HCl-15%	H	6,978,000	0.017	118,610
Thiodiglycol-67%	H	2,567,000	0.500	859,950
Total				1,500,000

* Estimated values--much higher values may be assumed if MPA is used to produce DF.

The value of the metal after incineration is not included since the same amount will also be produced from the baseline. A comparison of the hydrolysis process, including the cost of facilities and munition disassembly with the R&D baseline is given in the next section.

2.5.4.5.7 Comparison of Hydrolysis with the Baseline.

The cost/benefit data derived for the hydrolysis process are based on 1000 lb of agent per hour. The R&D baseline, however, is based on a capacity of 400 lb/hr. To compare hydrolysis with the baseline, we scaled the hydrolysis process to 400 lb/hr of agent. The equipment cost was adjusted using the following equation:

$$\text{Cost}_i = \text{Cost}_j \left[\frac{\text{size}_i}{\text{size}_j}\right]^{0.6}$$

The operating cost was adjusted differently. Total utility costs remained constant. Labor and spare parts increased because the duration of the project was increased from 0.85 to 2.87 years. The operating cost for the 400 lb/hr plant was calculated to be $3.37 million. The details are shown in Table 22 for the hydrolysis process. The operating cost of the incinerator in the 400 lb/hr plant was assumed to be the same as for the 1000 lb/hr plant.

TABLE 22. TOTAL ESTIMATED OPERATING COSTS OF HYDROLYSIS PROCESS PER SITE BASED ON 400 LB/HR OPERATION

Item	Cost, $
Raw Material	
Ethanol Amine	33,730
Dimethyl Sulfoxide	164,970
Utilities	
Electricity	8,070
Water	510
Fuel Oil	274,000
Fixed Costs	
Labor	2,235,000
Spare Parts	406,930
Total Operating Costs Excluding By-Product	3,123,210

The following assumptions were also made:

(1) The facility that will house the hydrolysis process is the same size as that which will house the process on which the baseline is based.

(2) The munition disassembly cost will be the same as the corresponding cost for the baseline system.

(3) The availability of hydrolysis will be the same as that of the baseline.

The total cost of the hydrolysis process was determined on the basis of these assumptions. The results are compared with the baseline in Table 23.

2.5.4.5.8 Observations on the Hydrolysis Process and Conclusions.

The technical and economic analyses performed on the hydrolysis process lead to the following conclusions:

(1) The process is straightforward and uses commercially available and easily scaleable equipment. Experiments are required to verify the kinetics which were either calculated or extrapolated from limited data.

(2) Savings of about $25 million may result from each site over the baseline for a total savings of $250 billion on the 10 sites. We believe the analysis is conservative, for example:

TABLE 23. COMPARISON OF THE HYDROLYSIS PROCESS WITH THE BASELINE BOTH BASED ON 400 LB OF AGENT PER HOUR

Cost Item	Munition Common Cost	Munition Disassembly Cost	Hydrolysis Baseline Process Specific Cost	Process Specific Cost	Total Total Baseline Cost	Chemical Process Cost*
Facilities	3.97	1.99	1.43	1.43	7.39	7.38
Equipment	10.44	2.83	21.44	2.47[+]	34.71	15.74
Operation	44.07	4.82	10.26	4.03**/ 2.54	59.15	52.93/ 51.43
Total	58.48	9.63	33.13	7.94/ 6.44	101.24	76.05/ 74.55

* Operation x/y x excluding by-products credit; y including by-products credit size plant scale-up is based on 0.6 power.

[+] Cost for 400 lb/hr plant = $(2.281 + 2.0) \times 10^6 (400/1000)^{0.6} = 2.47 \times 10^6$

** Operating cost for 400 lb/hr plant:

Hydrolysis process		= 3.123×10^6 (Table 15)
Incinerator labor (3 men x $50,000 x 2.87 yrs)		= 0.431×10^6
Utilities		= 0.010×10^6
Maintainence	(6% x 2.87 yrs x 2.0×10^6)	= 0.344×10^6
	Subtotal	= 0.785×10^6
Disposal		= 0.134×10^6
	Total	= 4.04×10^6

- Very low availability of the plant is assumed. An increase of as much as 20 percentage points in the availability is likely, as was discussed in Section 2.5.3.3.5.2 of this report. Increased availability will reduce operating time and thus reduce labor costs including those common to all processes.
- The assumed throughput of 400 lb/hr may not be the optimum for the hydrolysis process. Thus more cost savings may be achieved at the optimum size.
- Energy costs of the hydrolysis process may be reduced drastically by recovery of heat from the incineration of the explosives and using it in the hydrolysis process. No credit for that is assumed. This may be accomplished at a minimal capital expense simply by circulating the mixture which is to be hydrolyzed through the incinerator shell.

- We believe that $2 million for incinerating the explosives in a rotary kiln incinerator is high. A less expensive open hearth furnace could be adequate, making possible a savings of as much as $1 million.
- The equipment is standard chemical processing equipment which is easy to decontaminate and reuse in other manufacturing facilities. No credit is claimed in that.

(3) The hydrolysis method definitely warrants further investigation in the laboratory because its economic potential is great.

2.5.5 Engineering and Economic Evaluation of Pyrolysis

The same analytical procedure and approach that were applied for hydrolysis were used in pyrolysis.

2.5.5.1 Kinetics

2.5.5.1.1 Kinetics of Pyrolysis of GB

Cheselske et al.[26] reported that pyrolysis of GB is a first order reaction and that its rate constant in seconds can be calculated from the following relationship:

$$\log k = 8.19 - \frac{5078}{T}$$

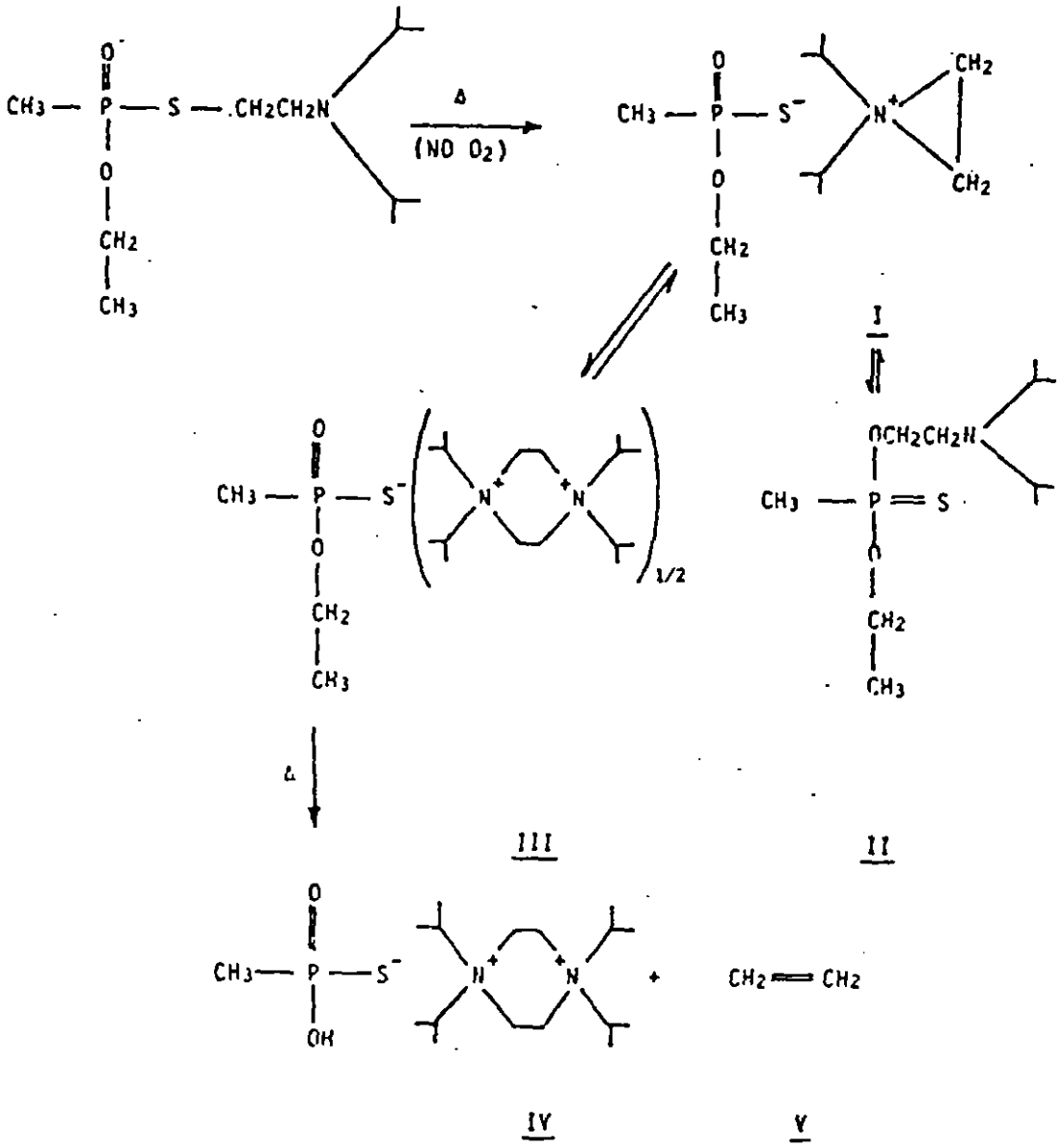
where T is in °K. This relationship is said to be valid in the 300°-400°C temperature range.

Taking the pyrolysis to be a first order reaction, we can calculate the required residence time for a given desired output concentration from the following relationship:

$$t = \frac{-\ln (1 - x_A)}{k}$$

where k is calculated from the equation. Using the two equations we can determine the residence time needed to reduce the GB concentration 10^9-fold. The results are shown in Table 24 and in Figure 6 as a function of temperature.

2.5.5.1.2 Kinetics of Pyrolysis of VX. In the case of VX, pyrolysis in the absence of oxygen produces a mixture of compounds I, II, III, IV, and V,[27] which are shown below:



I

II

III

IV

V

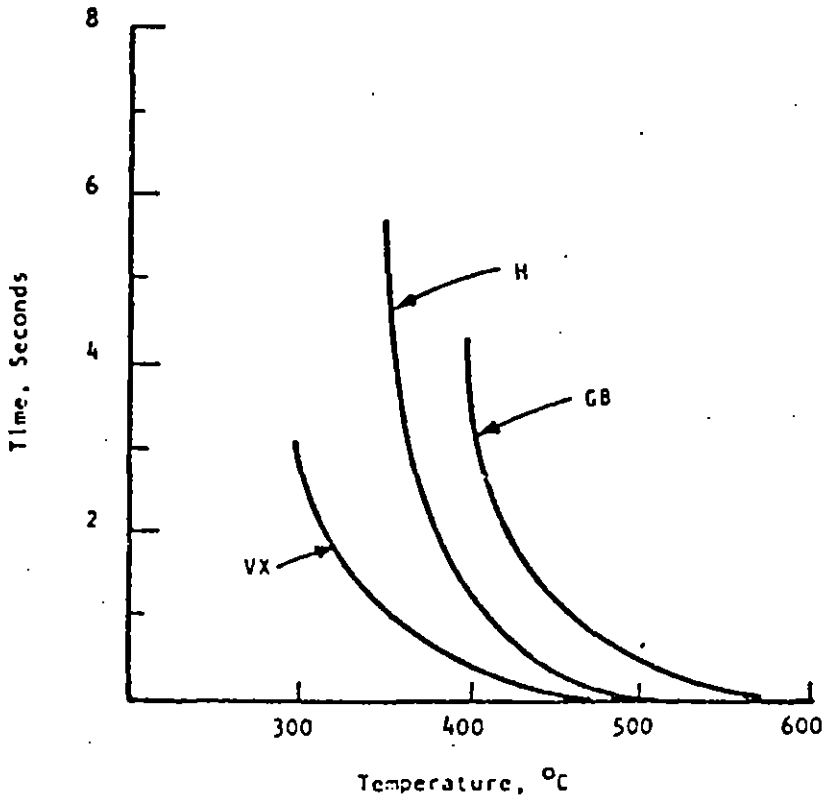


Figure 6. Dependence of the kinetics of the pyrolysis of the agents on temperature.

TABLE 24. REQUIRED RESIDENCE TIME FOR 10^9 FOLD DESTRUCTION OF GB BY PYROLYSIS

Temperature, °C	Residence Time, sec
300	75.74
400	3.65
450	1.10
560	0.13

Compound III will be the major product. This compound is not toxic; however, the conversion of I to III must be made quantitative because long-term storage of compound I could lead to the reformation of VX whereas compound III cannot. Landfilling is therefore not an acceptable method of disposing of III. Further processing of the products is required. The advantage of pyrolysis is the drastic reduction in the transportation cost. Product II is only a small side product from compound I.

The kinetics of the pyrolysis process of VX were discussed by R. R. Lapp and C. J. Schneider.[27] They established that the half-life may be calculated from the following relationship:

$$t_{1/2} = 10 \left(\frac{3800}{T} - 4.57\right)$$

where $t_{1/2}$ is in milliseconds and T is in °K. This relationship is valid in the temperature range 800°-1200°F (427°-649°C).

Using this relationship, we calculated the required residence time to reduce the concentration of VX 10^9 fold. The results are summarized in Table 25 and plotted in Figure 6.

2.5.5.1.3 Kinetics of Pyrolysis of H

The key products identified from the pyrolysis of H are hydrogen chloride, ethylene, ethylene dichloride, hydrogen sulfide, vinyl chloride, dithian, 2,2'-dichlorodiethyl disulfide, and non-volatile residue.[28] The ratio of these compounds in the product mix is a function of temperature. The author[28] also stated that the decomposition appeared complete at 450°C. At this temperature the nonvolatile residue constituted about 32 percent of the

TABLE 25. REQUIRED RESIDENCE TIME FOR DESTRUCTION OF VX BY PYROLYSIS TO THE PPB LEVEL IN A 2 MOLAR SOLUTION

Temp, °C*	Residence Time, sec
300	2.75
350	0.81
400	0.28
427	0.17
450	0.12
538	0.03
649	0.01
709	0.005
760	0.003

* Calculated data outside the valid range of the equation are used to help predict trend only.

total and contained about 45 percent of the sulfur and about 7 percent of the chlorine in the original feed. It is therefore very likely to contain compounds with vesicant properties. The other major compounds are hydrogen chloride (about 31.5 percent), vinyl chloride (about 19.4 percent), ethylene (about 10.4 percent), and hydrogen sulfide (about 5.2 percent). Vinyl chloride, ethylene, and hydrogen chloride have commercial applications if they can be separated; hydrogen sulfide must be scrubbed.

Cheselske et al.[26] established that the rate constant for the pyrolysis of mustard is:

$$\log (k) = 9.25 - \frac{5486}{T}$$

where k is seconds and T is °K. This relationship is valid in the temperature range 200°-400°C.

Using this relationship, we calculated the residence time required to reduce the concentration of H to the parts-per-billion level. The results are summarized in Table 26 and plotted in Figure 6.

The analysis of the three agents performed above leads to the following conclusions:

TABLE 25. REQUIRED RESIDENCE TIME FOR DESTRUCTION OF H BY PYROLYSIS TO THE PPB LEVEL

Temperature, °C	Residence Time, sec
200	35.94
300	34.3
350	5.8
400	1.3
450*	0.4

* Extrapolated

- Pyrolysis is rapid for all three agents at temperatures above 450°C.
- GB will produce useful products (MPA, MFPA, DF, and isopropyl alcohol). VX will result in products which require further processing, but which can be transported using conventional means to a central treatment plant.
- H produces useful products (vinyl chloride, HCl, ethylene), but scrubbing of the gaseous products from H pyrolysis could be a complex and costly process.

2.5.5.2 Process Description

Figure 7 is a simplified schematic diagram of the pyrolysis process. Agents are fed to the pyrolysis reactor and heated to the desired temperature. The residence time is controlled to reduce the concentration of the agent to the parts-per-billion level. The products are then cooled and flashed in a flash drum.

In the case of GB, propylene is produced and part of it is used to provide the thermal energy to the reactor. The process is thus energy self-sufficient except for its small electrical requirements. Excess propylene is collected and can be used as a fuel or as a feed stock. The liquid mixture which remains in the flash drum is primarily DF, MPA, and MFPA. Therefore it will be flashed again to recover the DF. The remaining MPA and MFPA can be processed further to produce DF via an anhydrous chlorinolysis process which is described separately in this report.

In the case of VX, flashing the mixture leaving the reactor produces small amounts of ethylene which may be mixed with the fuel used to heat the

Propylene (GB)
Ethylene (VX)
Scrubbers
Mixture (H)
DF (GB)
Anhydrous Chlorinolysis
Disposal
Water Soluble & Non Toxic Salts (VX)
MPA (GB)
MFPA (GB)
Medium P
Flash Drum
Gaseous Products
High P
Flash Drum
Liquid Mixture (H)
For Further Treatment
Air Cooler
Agent
Reactor
Heat Source

reactor. The remaining products are water-soluble and nontoxic compounds which could be disposed of by incineration.

Pyrolysis of mustard produces a mixture of gases and a large volume of nonvolatiles. The key products identified from pyrolysis are hydrogen chloride, ethylene, ethylene dichloride, hydrogen sulfide, vinyl chloride, dithian, 2,2'-dichlorodiethyl disulfide, and nonvolatile residue. The ratio of these compounds in the product mix is a function of temperature. At 450°C, the nonvolatile residue constitutes about 32 percent of the total and contains about 45 percent of the sulfur and about 7 percent of the chlorine in the original feed. It is therefore likely to contain compounds with vesicant properties. The other major compounds are hydrogen chloride (about 31.5 percent), vinyl chloride (about 19.4 percent), ethylene (about 10.4 percent), and hydrogen sulfide (about 5.2 percent). Vinyl chloride, ethylene, and hydrogen chloride have industrial uses if they can be separated; hydrogen sulfide must be scrubbed.

The fact that the nonvolatile mixture may have vesicant properties indicates that further processing is required. Separation of the gas mixture is also a complex process. Therefore we expect the pyrolysis of H to be a complicated and costly process.

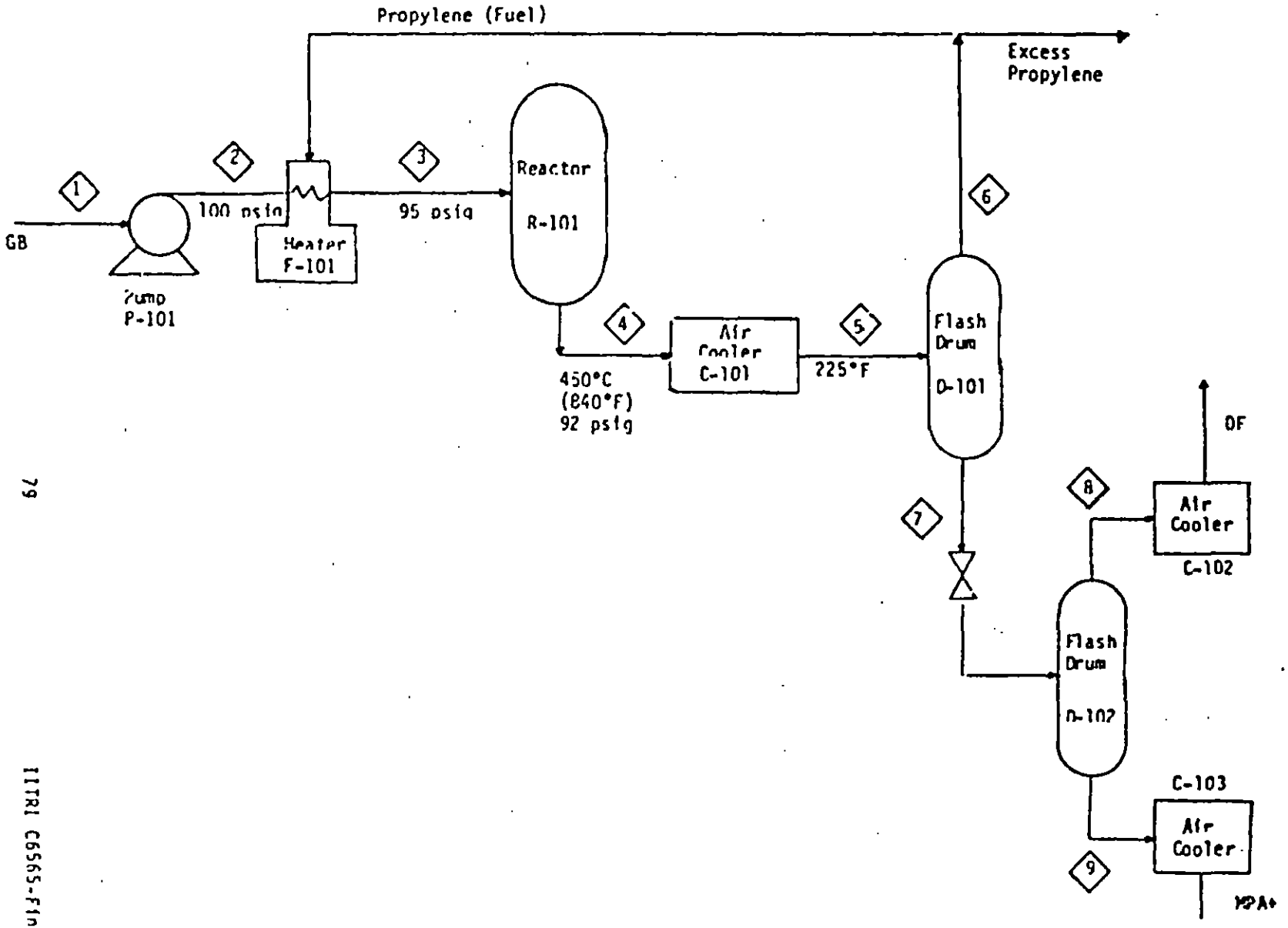
The details of the pyrolysis of the three agents are presented below.

2.5.5.2.1 Pyrolysis of GB

- GB $\xrightarrow{\Delta}$ Propylene + DF + MPA + MFPA .
- Pyrolysis will be carried out at 450°C.
- Propylene will be used as fuel; MPA and MFPA can be used to produce DF. Thus there are no waste products.

Process Description. Figure 8 is a schematic diagram for the pyrolysis of GB. The agent is pumped to a pressure of about 100 psig. (This is suggested in order to reduce the volume of the equipment downstream from the heater since the fluids will be in the vapor phase after heating.) The agent is then heated to about 450°C and fed to the reactor. The reactor simply provides additional residence time at the high temperature. Heating the agent inside the reactor instead of having a separate heater was also evaluated.

Because of the high temperature required, heating with steam was ruled out and electrical heating or direct firing of fuel will be required.



Electrical heating is expensive and large quantities will be required. Direct firing of fuel will complicate the design of the reactor and this reduces the reliability of the system. Thus the setup shown in Figure 8 was adopted.

We also examined briefly the possibility of using a suitable catalyst which could be used to facilitate pyrolysis at lower temperatures of about 200° to 250°C. Steam heating could be used at such temperatures and the heating coils could be built into the reactor. We are not aware of catalysts for each of the three agents and thus it was decided that Figure 8 is a more conservative design.

The pyrolysis products leave the reactor hot and under pressure. An air cooler is used to cool them down to about 225°F so that propylene can be separated. Some of the propylene is used as the heat source for the heater while the remainder can be used for district heating of the plant or sold as chemical feed stock. After separating the propylene, the remaining mixture is primarily DF, MPA, and MFPA. MPA and MFPA can be used to manufacture DF, which is one of the binary components. A process for converting these to DF (anhydrous chlorination), discussed in the next section, is independent of pyrolysis.

It is clear from the above discussion that all the products are useful and there is no disposal problem except for minor accumulation of some solids and carbonaceous material in the reactor. The process is also energy self-sufficient except for the small electric power consumption of the pump and the fans on the air cooler.

If pyrolysis of GB is to be practiced, it could be carried out at about 200°C. At this temperature the liquid product will be primarily MFPA, which can be converted to DF; the process itself, however, will be slower.

2.5.5.2.2 Pyrolysis of VX

- Main reaction and products are as shown in the kinetics discussion.
- Pyrolysis will be carried out at 450°C.
- Small amounts of ethylene will be produced and may be used internally. Other products are useless but nontoxic compounds.

Process Description. Figure 8 can also be used to describe the pyrolysis of VX except that flash drum D-102 will not be needed. The agent (VX) will be

pumped and heated as described for GB. The products are small amounts of ethylene and two nontoxic water-soluble compounds. The products have no industrial or military value. Small amounts of water may have to be added to prevent the recrystallization of the products in the reactor. The ethylene will be mixed with the fuel that is used in heater F-101. The products will be disposed of by transporting them to a waste management company for incineration. The products are similar in nature to the compounds produced by the hydrolysis of VX.

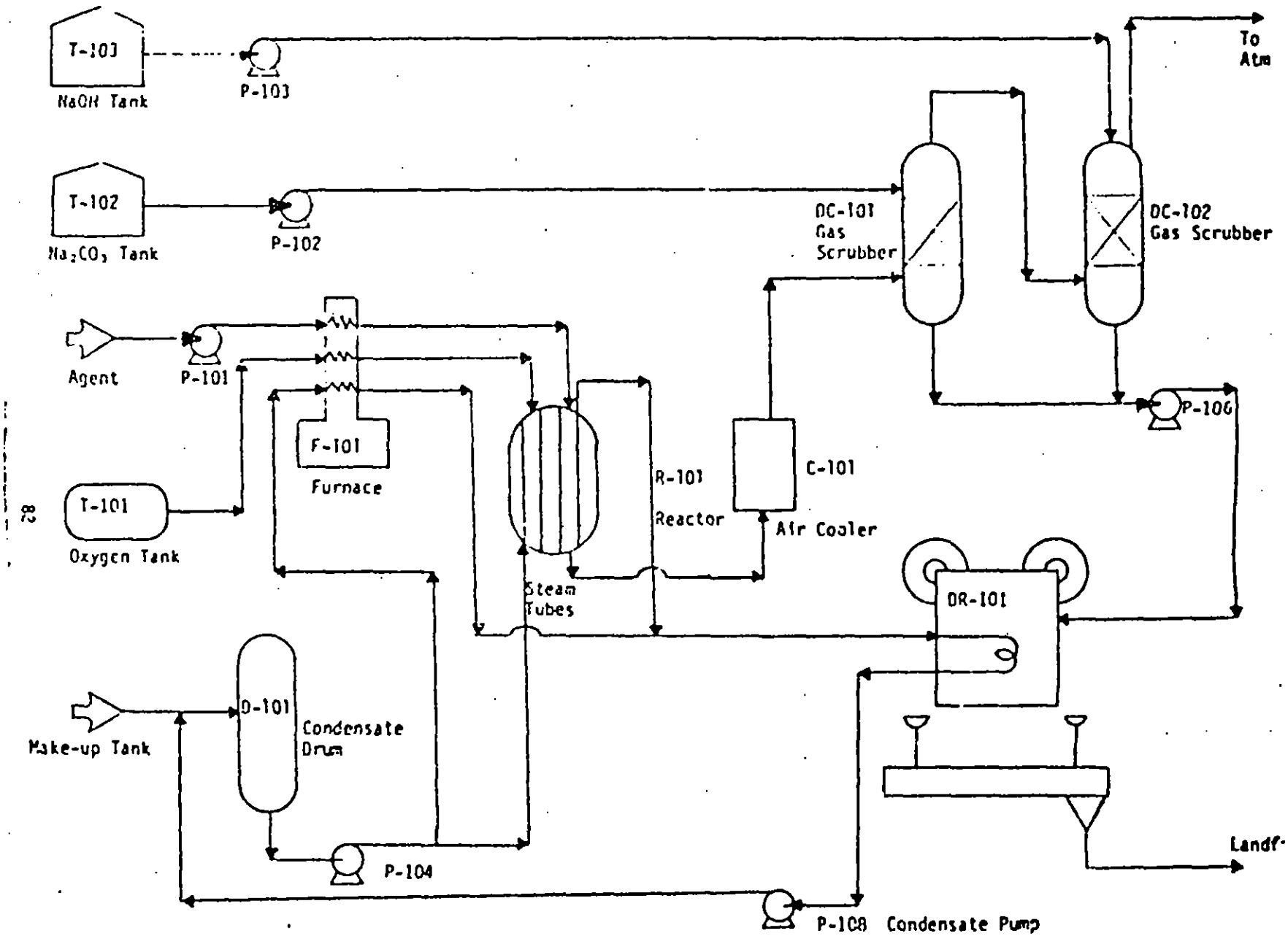
2.5.5.2.3 Pyrolysis of H

- Main reaction and products are as shown in the kinetics discussion.
- Pyrolysis will be carried out at 450°C.
- Gases that are costly to scrub will be produced.

Process Description. The pyrolysis of H can also be described by Figure 8. As the products enter flash drum D-101, a mixture of gases is separated from a large volume of nonvolatiles. The gaseous mixture contains three valuable products: hydrogen chloride (31 percent), vinyl chloride (19.4 percent), and ethylene (10.4 percent). The gaseous mixture also contains hydrogen sulfide (5.2 percent) and other impurities totaling about 2 percent. (The other 32 percent are the nonvolatiles.) Separation of the gas mixture to recover the useful products is very complex and costly since it requires methods such as cryogenic separation. Further, the nonvolatiles possess vesicant properties, and thus are difficult to dispose of.

Because of the above obstacles, we decided that pyrolysis of H is not an acceptable method as it stands. We modified the pyrolysis of H by introducing oxygen with the H to thermally oxidize it all the way to SO_2 and CO_2. The chlorine atoms are converted to HCl. Both SO_2 and HCl have to be scrubbed. The scrubbing process complicates the design and increases the cost significantly.

The conceptual design for the modified pyrolysis/thermal oxidation of H is shown in Figure 9. H is pumped through the furnace to be heated to the desired temperature and then fed to the reactor. An oxygen stream containing about 2 percent nitrogen is also preheated separately and fed to the reactor. Because of the large heat of reaction expected from the oxidation of mustard, the reactor is equipped with cooling coils through which water is


T-103
NaOH Tank
P-103
To Atm
T-102
Na_2CO_3 Tank
P-102
DC-101 Gas Scrubber
DC-102 Gas Scrubber
Agent
P-101
P-106
F-101
Furnace
T-101
Oxygen Tank
R-101
Reactor
C-101
Air Cooler
Steam Tubes
DR-101
Make-up Tank
D-101
Condensate Drum
P-104
P-108 Condensate Pump
Landf

converted to steam. The heat recovered from the reactor is used in drying the scrubbing product. The cooling coils will increase the cost of the reactor, but the reactors are commercially available. The products leaving the reactor consist of HCl, SO_2, H_2O, and CO_2. HCl and SO_2 need to be scrubbed. A system similar to the one used at CAMDS is incorporated in the design shown in Figure 9 for this purpose. The products are first cooled and then transferred to gas scrubber DC-101 where SO_2 and some HCl are scrubbed by an Na_2CO_3 solution via the following reactions:

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

$$Na_2CO_3 + H_2SO_3 \longrightarrow Na_2SO_3 + CO_2 + H_2O$$

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$$

The Na_2SO_4 (aqueous) is collected from the bottom of DC-101. The gases leaving DC-101 are sent to scrubber DC-102 for further scrubbing with NaOH. HCl is scrubbed via the reaction:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

The salt solution is mixed with the Na_2SO_4 brine and both are sent to the dryer to be dried since they contain large amounts of water and thus constitute a large volume for disposal. Drying is accomplished by steam which is raised by heat recovery from the reactor. The salts (Na_2SO_4 and NaCl) are agent free since they have been through several chemical treatment steps, and therefore can be landfilled.

The only two advantages that we see for this thermal oxidation method over incineration are:

(1) It uses equipment that is common to the pyrolysis of GB and VX. However, it also introduces new equipment primarily for scrubbing of the gases, which will make the whole system very expensive.

(2) It makes the pyrolysis process applicable to all three agents.

investment of large capital in equipment that will be used for a short period of time may not be a good business move. These disadvantages tend to suggest that pyrolysis is not a good approach. However, pyrolysis of GB is the first step toward converting GB to DF which is expensive and badly needed by the military because of the difficulty in finding suppliers. Further, the same equipment that is used for pyrolysis of GB can be used for the demilitarization of VX. Consequently, we selected the following hybrid system for evaluation: pyrolysis of GB and VX as described in Figure A and a furnace on site to incinerate the explosives, metals, and mustard.

2.5.5.3 Material and Energy Balances

Material and energy analyses were performed on Figure A for both GB and VX on the basis of 1000 lb of agent per hour. The results of the material balances are summarized in Tables 27 and 28 for GB and VX, respectively. The energy analysis was limited to estimating the duty of the heaters and coolers so that they could be sized. The results were used to establish the design values for these heaters and coolers as follows:

TABLE 27. MATERIAL BALANCE FOR PYROLYSIS OF GB (lb/hr)

Compound	MW	Stream Number								
		1	2	3	4	5	6	7	8	9
GB	140.1	1,000	1,000	1,000	--					
Propylene	42.1				300	300	300			
MFPA	~98.0				640	640		640		640
HPA	~96.0				30	30		30		30
DF	~100.0				30	30		30	30	
		1,000	1,000	1,000	1,000	1,000	300	700	30	670
	T(°F)	80	80	842	842	225	225	225	225	225
	P(psia)	0	100	95	92	87	85	85	70	70

Assumptions: LHC Propylene = 19,683 Btu/lb

Total heat in propylene combustion = 19,683 Btu/lb x 300 lb/hr = 5,904,900 Btu/hr.

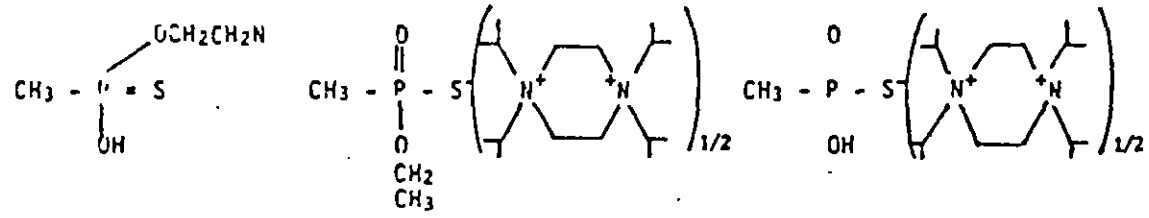
No steam is generated if not used in the process.

TABLE 28. MATERIAL BALANCE FOR PYROLYSIS OF VX (lb/hr)

Basis--1,000 lb/hr

	Stream Number								
	1	2	3	4	5	6	7	10*	11*
VX	1,000	1,000	1,000	--	--				
Ethylene				10	10	10			
Compound 1				45	45		45		45
Compound 2				900	900		900		900
Compound 3				45	45		45		45
Water							600	600	600
	1,000	1,000	1,000	1,000	1,000	10	1,590	600	1,590
T (°F)	80	80	842	842	400	220	220	90	120
P (psig)	0	100	95	92	87	87	87	85	80

Compound 1 (5%) Compound 2 (90%) Compound 3 (5%)



* Streams 8 and 9 are all zeros. Stream 10 water is added to solubilize salts for easy handling, same ratio as hydrolysis waste which has about 8000 Btu/lb heating value.

Heater F-101	850,000 Btu/hr
Cooler C-101	700,000 Btu/hr
Cooler C-102	50,000 Btu/hr
Cooler C-103	100,000 Btu/hr

Heat transfer coefficients were estimated because of the lack of adequate data in literature.

2.5.5.4 Design Criteria of the Pyrolysis System

Table 29 summarizes the design criteria which were established for the equipment shown in Figure 8.

TABLE 29. DESIGN CRITERIA FOR MAJOR PYROLYSIS EQUIPMENT

Equipment	Specifications	Material
P-101	2.5 gpm, 0.5 hp	Carbon steel
P-102	1.5 gpm, 0.2 hp	Stainless steel
D-101	1'ϕ x 6'L	Stainless steel
D-102	1'ϕ x 5'L	Stainless steel
C-101	700 MBtu/hr	Stainless steel
C-102	50 MBtu/hr	Stainless steel
C-103	100 MBtu/hr	Stainless steel
T-101	1,500 gal	Carbon steel
T-102	30,000 gal	Stainless steel
R-101	2'-0" ϕ x 2'-0" L	Stainless steel
F-101	850 MBtu/hr	Stainless steel

2.5.5.5 Economic Evaluation

The economic evaluation procedure adopted for this process is similar to that used for hot water hydrolysis, except that the cost of the furnace which is used to incinerate mustard, explosives, and metals was estimated relative to the R&D baseline. The details are discussed below.

2.5.5.5.1 Capital Equipment Cost of the Pyrolysis Process of GB and VX

The installed cost of each of the components shown in Table 29 was estimated and reported in Table 30 below.

The total installed cost is $ 171,000. This does not include the cost of the small valves which are included in the cost of piping. Cost of piping is assumed to be 25 percent of the total installed cost. An additional 25 percent is added for design, hence:

Total equipment installed cost	= $ 171,100
Piping cost (25 percent)	= $ 42,800
Design (25 percent)	= $ 53,500
Total process installed cost	= $ 267,400

The equipment and installation costs are very small. This is encouraging since, if GB is pyrolyzed and the products are chlorinated to produce DF, the cost of the pyrolysis portion will be small.

TABLE 30. INSTALLED EQUIPMENT COST ($ 1982)

Item	Installed Cost, $
P-101	4,600
P-102	4,100
D-101	5,400
D-102	5,400
C-101	15,000
C-102	3,800
C-103	6,200
T-101	11,600
T-102	52,800
R-101	24,200
F-101	38,000
Total	171,100
Piping Cost (25%)	42,800
Design Cost (25%)	53,500
Total Plant Installed Cost	267,400

2.5.5.5.2 Operating Cost of the Pyrolysis Process of GB and VX

The operating cost of the pyrolysis process is summarized in Table 31.

Pyrolysis of VX will also produce 508,800 lb of product solution or about 61,000 gal. Since the products are similar in nature to those produced by the hydrolysis process, we can estimate the cost accordingly, i.e.:

Cost of incinerating 67,000 gal of VX waste from hydrolysis = $ 133,750

Cost of incinerating 61,000 gal of VX waste from pyrolysis (by a commercial waste disposer) = $ 121,770

2.5.5.5.3 Cost of an Incineration Process for Mustard, Explosives, and Metals

The R&D baseline process-specific cost is $ 33.10 x 10^6. The cost of the proposed incineration facilities, assuming H is 60 percent of stockpile, is $24.4 x 10^6 [$33.10 x $(0.6)^{0.6}$]. This number is based on a plant capacity of about 400 lb/hr, and does not include the facility and munition disassembly cost for the complete hybrid process.

2.5.5.5.4 Total Cost

The total process-specific cost of the pyrolysis of GB and VX is about $600,100, based on 1000 lb/hr of agent plant capacity:

TABLE 31. OPERATING COSTS BASED ON (1000 lb/hr OPERATION) OF THE PYROLYSIS OF GB & VX (0.34 Years)

Item	Consumption	Cost, $
Raw Materials		0
Utilities		
Electricity	4,080 kWhr	204
Water	23,040 gal	14
Fuel Oil	1,030 gal	1,240
Fixed Costs		
Labor 4 men/shift, 3 shifts, $ 50,000		204,000
Spare parts 6% of capital		5,455
Process-Specific Total Operating Costs		210,900

Installed plant cost	= $ 267,400
Operating cost	= $ 210,900
Disposal cost	= $ 121,800
Total cost	= $ 600,100

This total excludes the total cost of the incinerator for mustard, explosives, and metals.

2.5.5.5.5 Comparison of Pyrolysis/Incineration Hybrid with RAD Baseline

The cost data derived for the pyrolysis process are based on 1000 lb of agent per hour. To compare pyrolysis with the baseline, we scaled the pyrolysis process to 400 lb/hr of agent. The equipment cost was adjusted using the following equation:

$$\text{Cost}_i = \text{Cost}_j \left[\frac{\text{size}_i}{\text{size}_j}\right]^{0.6}$$

This resulted in a total installed cost for the 400 lb/hr plant of $154,300. The operating cost was adjusted differently. Total utility costs remained constant. Labor and spare parts increased because the duration of the project was increased from 0.34 to 1.15 years. The operating cost for the 400 lb/hr pyrolysis plant was calculated to be 0.864 million dollars. The details are shown in Table 32.

TABLE 32. OPERATING COSTS OF THE PYROLYSIS PROCESS BASED ON 400 LB/HR OPERATION

Item	Cost, $
Raw Material	0
Utilities	
Electricity	204
Water	14
Fuel Oil	1,240
Fixed Costs	
Labor (Assuming same number of men)	690,000
Spare Parts	18,450
Total Operating Costs Excluding By-Product	709,900
Total Operating Cost and Installed Cost	864,200

The total process-specific cost of a 400 lb/hr hybrid plant is therefore $25.26 million, i.e.

Pyrolysis	= $ 0.864 x 10^6
Incineration	= $ 24.4 x 10^6
Total	= $ 25.26 x 10^6

The common cost and the cost of munition disassembly is expected to be the same as for the baseline.

2.5.5.5.6 Observations on the Hybrid Process and Conclusions

The technical and economic analyses performed on this process lead to the following conclusions:

(1) The process is straightforward and uses commercially available, proven, and easily scaleable equipment. Experiments are required to verify the kinetics which were either calculated or extrapolated from limited data.

(2) Pyrolyzing GB and VX instead of incinerating them will simplify the incinerator design since the problems associated with the scrubbing of P_2O_5 are greatly reduced. Pyrolysis of GB will also produce MFPA which can be used to produce DF.

(3) Potential savings of $7.8 million per site over the baseline are estimated. The pyrolysis of GB will also produce DF, MPA, and MFPA, which may be converted to 685,000 lb of DF, with a market value of about $28/lb. It is therefore

a waste of millions of dollars to incinerate GB. In addition, it may not be easy to find a supplier of DF.

2.5.6 Engineering and Economic Evaluation of Anhydrous Chlorinolysis

Anhydrous Chlorinolysis is attractive because it produces very valuable products. GB and VX are converted to DF which can be used in binary munitions. H can be converted to S_2Cl_2, HCl, and $ClCH_2$-CCl_3. Furthermore, all the reactions can be carried out at ambient conditions using inexpensive and commercially available equipment. This method gives the Army the capability to produce and stock large amounts of DF. This is important because there are currently no suppliers for this material. This method was therefore selected for engineering and economic evaluation. The details of the evaluation are presented below for each of the three agents.

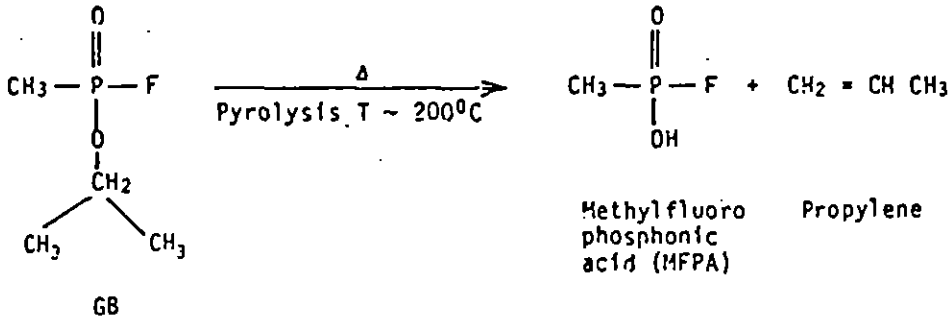
2.5.6.1 Kinetics

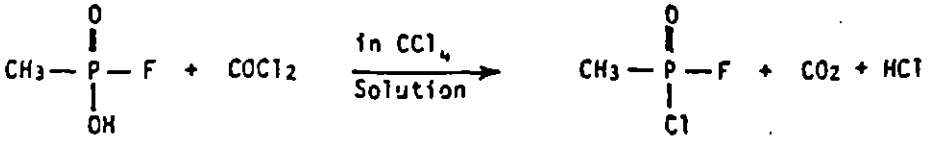
No information on the kinetics of anhydrous chlorinolysis was identified in our literature search. We estimated a conservative reaction time of 3 hours for equipment sizing. We believe that 1-2 hours could be enough at ambient conditions. Should more time be required for complete reaction its impact on our analysis will be small.

2.5.6.2 Process Description

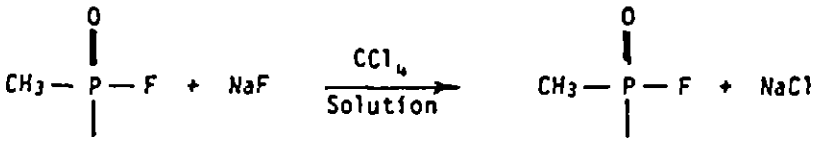
2.5.6.2.1 Anhydrous Chlorinolysis of GB

- The main reactions for the conversion of GB to DF via this method are:





MFPA Phosgene Methylphosphonic chlorofluoride



Methylphosphonic chlorofluoride Sodium fluoride DF

- Except for the pyrolysis step, the reactions are expected to take place at room temperature and pressure.
- HCl and DF are both usable products.
- Relatively small amounts of NaCl (0.4 lb NaCl/lb GB) will be produced. Since the GB would have gone through several processing steps by then, it can be assumed to be agent free and thus can be landfilled. Incineration is selected, however, because it may contain CCl_4.

The pyrolysis step is similar to the pyrolysis process described in Section 2.5.2.5. This section will therefore address only the processing of MFPA to produce DF.

Figure 10 is a flow diagram of this process. A mixture of MFPA and carbon tetrachloride is pumped to reactor R-101. When a sufficient batch quantity of the mixture is accumulated in the reactor, phosgene gas is bubbled through the mixture at a flow rate to limit the reactor temperature rise. Air cooler C-101 is used to cool the reactor, since the reaction with phosgene is exothermic. The temperature in the reactor is further controlled by recirculating the solution in the reactor using pump P-103. Recirculation also provides proper mixing of the reactor contents. Gaseous products are continuously removed (stream 4) and scrubbed with water.

When the reaction is complete (MFPA + methyl phosphonic chlorofluoride), the reactor liquid (methyl phosphonic chlorofluoride) is transferred to a

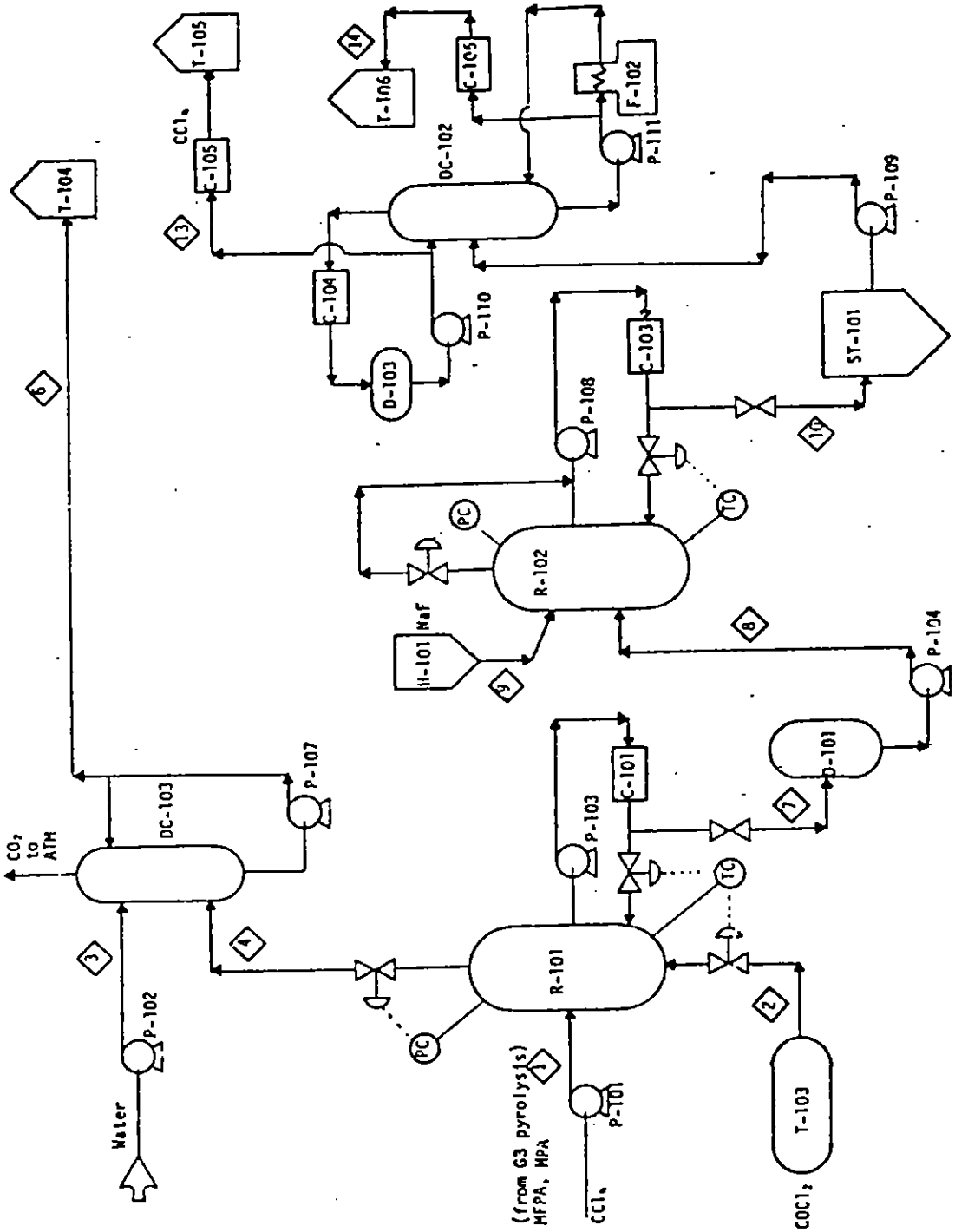


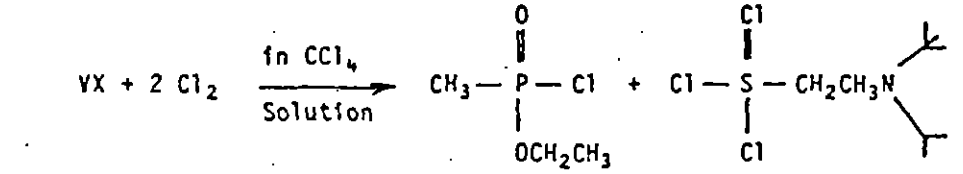
Figure 10. Process flow diagram for anhydrous chlorinolysis of GB.

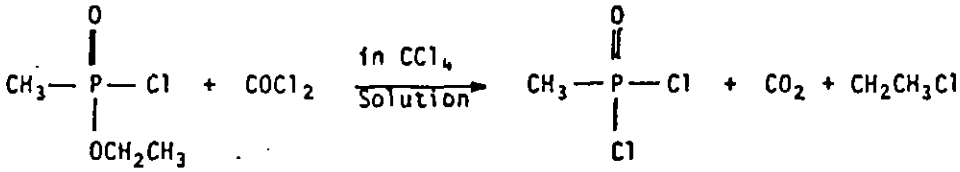
holding drum. Every 3 hours the content of the holding drum is pumped to reactor R-102. There, sodium fluoride is added through lockhopper H-101 so that it may be converted to DF. The resulting by-product is sodium chloride. The addition of NaF is regulated by the reactor temperature. Circulation of the contents using pump P-108 also helps regulate the temperature and provide mixing of the reactants. The reaction is expected to be complete in about 3 hours. At that point the products are pumped into a settling tank to remove sodium chloride. The overflow containing DF and CCl_4 is continuously fed to distillation column C-102 to boil off CCl_4. Air coolers C-105 and C-106 are used to cool the overhead product (CCl_4) and the bottom product (DF), respectively.

2.5.6.2.2 Anhydrous Chlorinolysis of VX

Of all the methods considered, this is the only method that can produce useful products from VX. A three-step process is expected to convert the VX to DF.

- The main reactions for the conversion of VX to DF via this method are:





- All these reactions can be carried at room temperature and atmospheric pressure.
- The binary agent DF is produced. Other reaction by-products are disposed of by a waste management organization.

Figure 11 is a flow diagram of this process. A mixture of VX and carbon tetrachloride is pumped via pump P-101 to reactor R-101. When a sufficient batch quantity of the mixture (~3 hours batch) is present in the reactor, chlorine gas is bubbled through it. The flow rate of chlorine is controlled by the reactor temperature. The heat of reaction is removed from the reactor by a recirculating side stream which is cooled by cooler C-101. Recirculating pump P-103 is used to control the reactor temperature and to provide good mixing in the reactor. This reaction may take about 3 hours to complete. Reactor pressure is controlled by recycling undissolved chlorine with the recirculating liquid, thus forcing chlorine to dissolve and react in the liquid phase.

The products of reactor R-101 are then transferred to holding drum D-101. A continuous stream (5) is pumped via pump P-104 to distillation column DC-101, where the bottom product (stream 7) is cooled (C-107) and stored in tank T-107. The overhead product (stream 6) is stored in reflux drum D-102.

Upon availability of reactor R-102, the contents of D-102 drum are fed to reactor R-102 until a sufficient batch quantity (~3 hours batch) is present in the reactor. First, the phosgene gas stream (3), controlled by the reactor temperature, is bubbled into the reactor for about 3 hours. Gaseous products are continuously removed from the reactor and are scrubbed by ethanol in column DC-103. The scrubber bottoms are pumped to storage tank T-104. Sodium fluoride is added from lockhopper H-101. Recirculating pump P-108 is used to control the reactor temperature and provide adequate mixing in the reactor.

After about 3 hours of reaction with NaF (~6hours total), the reaction is expected to be complete. The products are then pumped from reactor R-102

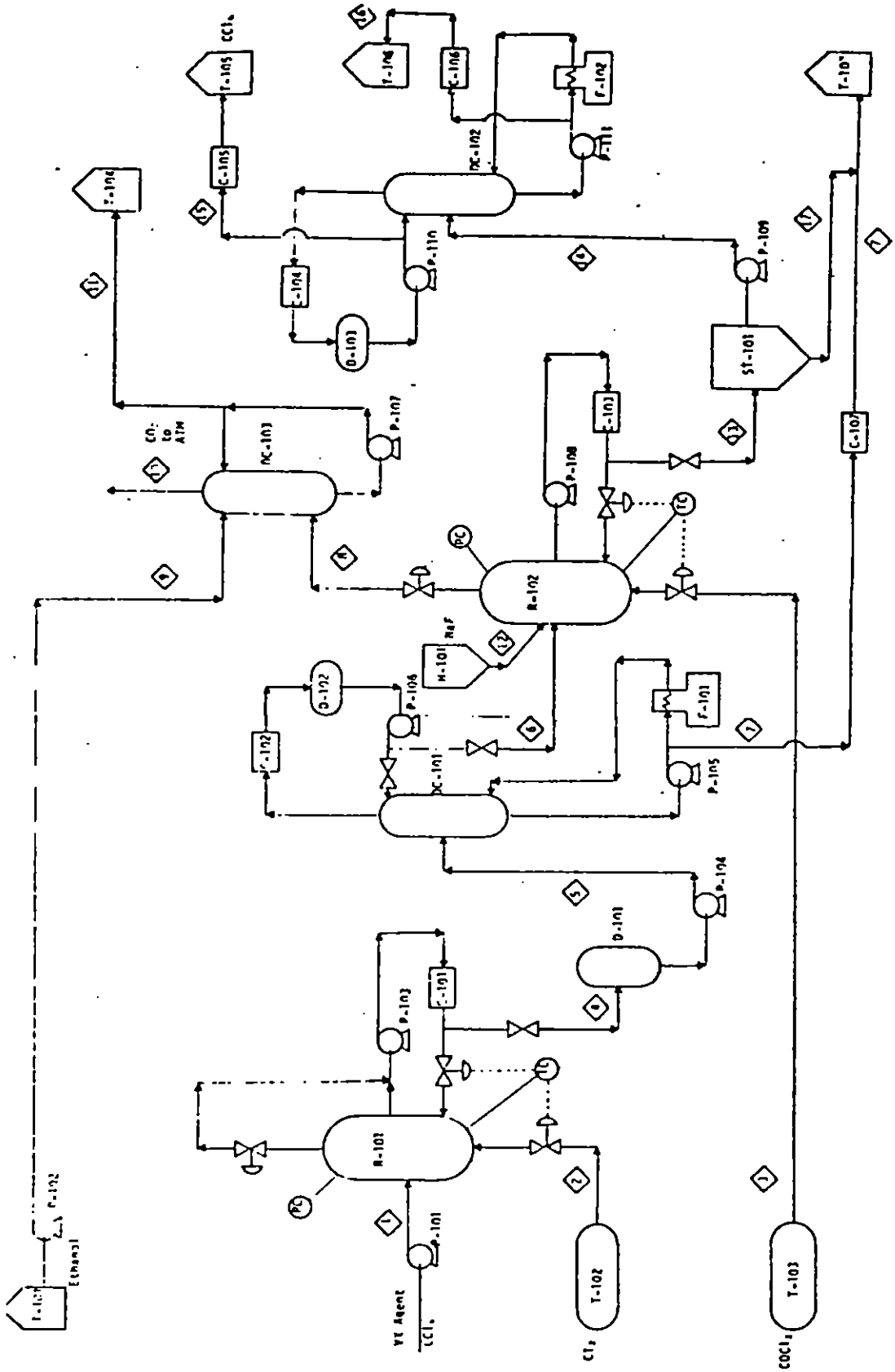


Figure 11. Process flow diagram for anhydrous chlorinolysis of VX.

to a settling tank where sodium chloride (stream 17) is removed. The overflow (stream 14) is continuously fed to a distillation column where carbon tetrachloride is separated from DF. The overhead product (CCl_4) and the bottom products (DF) are cooled by air coolers C-105 and C-106, respectively.

Two reactions take place in reactor R-102. The alternative was to install two reactors, one for each reaction. Preliminary economic analysis of the two alternatives was performed and a one-reactor system was selected over purchasing an extra reactor since VX constitutes only about 10 percent of the stockpile.

2.5.6.2.3 Anhydrous Chlorinolysis of H

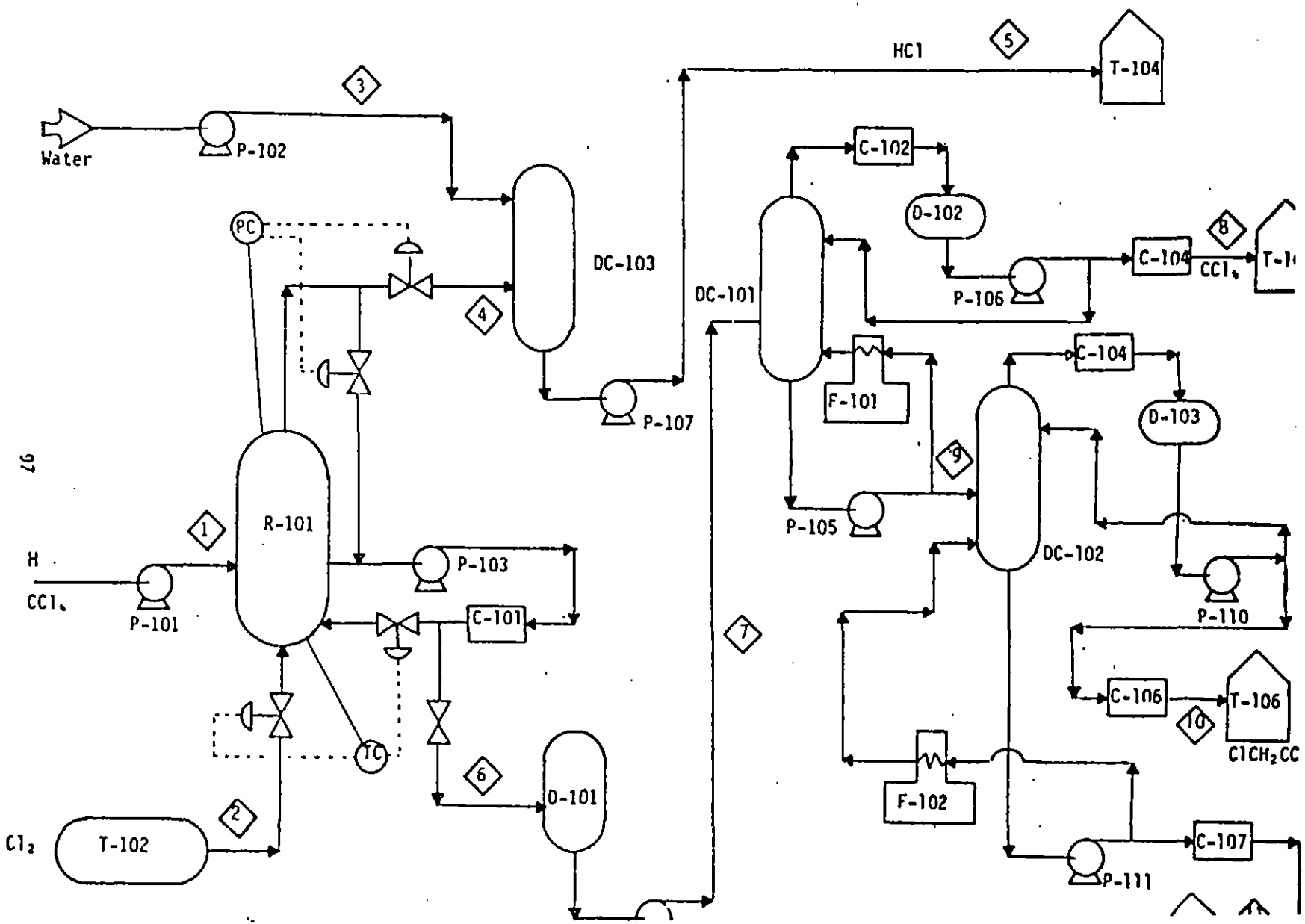
- The major reaction is

$$2(\text{Mustard}) + 11(Cl_2) \xrightarrow[\text{Solution}]{\text{in } CCl_4} 4\ ClCH_2 - CCl_3 + S_2Cl_2 + 8\ HCl$$

- The above reaction will be carried out at room temperature and atmospheric pressure.
- HCl, tetrachloroethane, and sulfur dichloride are all salable products. There are no waste products.

Figure 12 is a flow diagram of this process. A mixture of mustard and carbon tetrachloride is pumped (P-101) from the munition washing area tank to reactor R-101. When a sufficient batch quantity of the mixture (~3 hours batch) is present in the reactor, chlorine gas, the flow of which is controlled by the reactor temperature, is bubbled into the reactor. The heat of reaction is removed from the reactor by a recirculating side stream which is cooled by cooler C-101. Recirculating pump P-103 is used to control the reactor temperature and provide adequate mixing in the reactor. The gaseous product (stream 4) is removed continuously from the reactor and scrubbed by DC-103 with water. The bottom product from the scrubber is a hydrogen chloride solution and is stored in storage tank T-104 for sale.

The product of reactor R-101 is then pumped to holding drum D-101. A continuous stream (7) is fed to distillation column DC-101, where CCl_4 is distilled off as the overhead product. The bottom product (stream 9) is fed to distillation column DC-102. The overhead product, which consists of tetrachloroethane, is pumped (P-111) to storage tank T-106 after being cooled by air cooler C-106. The bottom product is S_2Cl_2. It is also cooled and stored in tank T-102.


Water
P-102
3
HCl
5
T-104
C-102
D-102
C-104
8
CCl4
T-1
P-106
PC
DC-103
4
DC-101
F-101
C-104
D-103
9
P-107
P-105
DC-102
R-101
1
H
CCl4
P-101
P-103
C-101
P-110
C-106
T-106
10
ClCH2CC
TC
6
D-101
7
F-102
2
Cl2
T-102
C-107
P-111

A comparison of Figures 10, 11, and 12 reveals that most components of the three configurations are common to all three agents. Thus a list of equipment was included so that the basic system could be used for all three agents. All equipment needed by any of the three agents is added to the list. This is presented later in the discussion on the economics of the system.

2.5.6.3 Material and Energy Balances

Material and energy analysis were performed on the three configurations (B1, B2, and B3) based on an agent flow rate of 1000 lb per hour. The results from the material balance analysis are summarized in Tables 33, 34, and 35 for GB, VX, and H respectively. The energy balance analysis was restricted to estimates of the duty of the air cooler in the process diagrams in order to determine its relative size and cost. The results are summarized in Table 36.

2.5.6.4 Design Criteria of the Anhydrous Chlorination System

The following criteria and constraints were adopted for the plant which will treat all of the three agents:

- Plant must process all three agents. Thus equipment designs are based on the largest flow rate and/or heat duty required in any of the cases.
- All reactions are carried out at room temperature and atmospheric pressure.
- Agent concentration in the process feed corresponds to 1 molar in the carbon tetrachloride solvent.
- Residence time of 3 hours is set for each reaction.
- Due to the complexity of gas/liquid reactions, all reactors are designed for batch operation. All other equipment are operated continuously.
- 1000 lb/hr of agent was adopted as the design basis.
- No fractionation losses.
- Chlorine and phosgene are very soluble in carbon tetrachloride.
- Sodium chloride can be precipitated from the organic solvents.

Based on the above criteria, the essential equipment was sized as shown below.

TABLE 33. MATERIAL BALANCE FOR ANHYDROUS CHLORINOLYSIS OF GB
(1000 lb/hr GB Average Flowrate)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14
MFPA, MPA*	700													
CCl_4	11,393						11,393	11,393		11,393		11,393	11,393	
$COCl_2$		707												
CO_2				314	314									
HCl				261		261								
H_2O			317			317								
MPClF**							832	832						
NaF									300	0				
NaCl										418	418			
DF										714		714		714
Total	12,093	707	317	575	314	578	12,225	12,225	300	12,525	418	12,107	11,393	714

* Small amounts of MPA

** MPClF (Methyl phosphonic chlorofluoride)

TABLE 34. MATERIAL BALANCE FOR ANHYDROUS CHLORINOLYSIS OF VX
(1000 lb/hr VX Average Flowrate)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
VX	1000																
CCl_4	5974			5974	5974	5974							5974	5974	5972		2
Cl_2		531															
$COCl_2$			370														
EMPCl*				534	534	534											
Comp. 1**				997	997		997										
Ethanol									121		121						
CO_2								65		165							
Chloroethane Dichloride								242			242						
HaF												315					
NaCl													438				438
DF													375	375		375	
Total	6974	531	370	7505	7505	6508	997	307	121	165	363	315	6787	6349	5972	375	440

* EMPCl (Ethylmethyl phosphonochloridate)

** Comp. 1

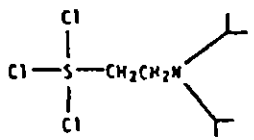


TABLE 35. MATERIAL BALANCE FOR ANHYDROUS CHLORINOLYSIS OF H
(1000 lb/hr H Average Flowrate)

Compound \ Stream	1	2	3	4	5	6	7	8	9	10	11
H	1,000										
CCl_4	10,026					10,026	10,026	10,026			
Cl_2		2,452									
$ClCH_3CCl_3$						2,110	2,110		2,110	2,110	
S_2Cl_2						424	424		424		424
HCl				917	917						
H_2O			1,114		1,114						
Total	11,026	2,452	1,114	917	2,031	12,560	12,560	10,026	2,534	2,110	424

TABLE 36. ANHYDROUS CHLORINOLYSIS EQUIPMENT LIST

Equipment	Design Criteria and Size	Material of Construction
Tank:		
T-101	6000 gal	C.S.
T-102*	9'ϕ x 27'L	S.S.
T-103*	6'ϕ x 18'L	S.S.
T-104	100,000 gal	S.S.
T-105	25,000 gal	Hastelloy B
T-106	100,000 gal	Hastelloy B
T-107	50,000 gal	S.S.
Pump:		
ST-101	5500 gal	Hastelloy B
P-101	230 gpm, 4.2 hp	Hastelloy B
P-102	2.8 gpm, 0.1 hp	Hastelloy B
P-103	240 gpm, 4.3 hp	Hastelloy B
P-104	20 gpm, 0.6 hp	Hastelloy B
P-105	7.5 gpm, 0.4 hp	Hastelloy B
P-106	19 gpm, 0.5 hp	Hastelloy B
P-107	5 gpm, 0.2 hp	Hastelloy B
P-108	235 gpm, 6.5 hp	Hastelloy B
P-109	19 gpm, 0.5 hp	Hastelloy B
P-110	21.4 gpm, 0.4 hp	Hastelloy B
P-111	23.5 gpm, 0.5 hp	Hastelloy B
Reactor:		
R-101	6100 gal	Hastelloy B
R-102	6100 gal	Hastelloy B
Drum:		
H-101	25 ft^3	C.S.
D-101	7'-3'ϕ x 21'9"L	Hastelloy B
D-102	3'-6"ϕ x 14'L	Hastelloy B
D-103	3'-6"ϕ x 14'L	Hastelloy B

TABLE 36. ANHYDROUS CHLORINOLYSIS EQUIPMENT LIST (continued)

Equipment	Design Criteria and Size	Material of Construction
Cooler:		
C-101	800 MBtu/hr	Hastelloy B tubes
C-102	1.25 MMBtu/hr	Hastelloy B tubes
C-103	800 MBtu/hr	Hastelloy B tubes
C-104	1.4 MMBtu/hr	Hastelloy B tubes
C-105	800 MBtu/hr	Hastelloy B tubes
C-106	225 MBtu/hr	Hastelloy B tubes
C-107	50 MBtu/hr	Hastelloy B tubes
Heater:		
F-101	1.6 MMBtu/hr	Hastelloy B tubes
F-102	1.8 MMBtu/hr	Hastelloy B tubes
Column:		
DC-101	2'ϕ, 30' packing	Hastelloy B
DC-102	2'ϕ, 30' packing	Hastelloy B
DC-103	1'ϕ, 20' packing	Hastelloy B

* 7 tanks of each type are needed to provide storage for 15 days of operation

- Reactors. Due to the complexity of gas/liquid reactions, designed to operate batchwise. Three hours residence time is needed in reactors R-101 and R-102. Reactors R-101 and R-102 are sized for 3-hours holding. Reactor R-102 is to operate 3 hours for the $COCl_2$ reaction and 3 more hours for NaF reaction in the VX case. This is done to avoid purchasing a new reactor. Preliminary economic evaluations forced this configuation since VX constitutes only 10 percent of the total available agent.
- Drums. Sized based on the inlet flow rates, except for D-101 and D-102, which are designed to hold 6 hours volume.
- Coolers. Sized based on the largest heat duty encountered upon processing any of the 3 agents. Air coolers are used instead of the cheaper water coolers for the same reasons stated in the discussion of the hydrolysis process.
- Tanks. Designed for a 15-day storage under full-load operations.
- Columns. Vapor/liquid equilibrium data needed for actual design of the columns are not available. Most equilibrium data correlations do not apply for the agents, solvents, and/or by-products involved in this process, and thus relevant data will have to be generated experimentally. Experimental work is beyond the scope of this phase. Therefore, a conservative engineering judgment is used to size all the columns.

Based on the above criteria, a list of all equipment needed to process the three agents was prepared (Table 36).

Except for the gas/liquid contacting, the nonaqueous chlorinolysis process is simple. It can be used to destroy all three agents and produce the binary DF from both GB and VX. It is technically feasible if the postulated reactions can go to completion. An economic evaluation of nonaqueous chlorinolysis is presented below.

2.5.6.5 Economic Evaluation

Economic evaluation of this method was carried out in a fashion identical to that for hydrolysis. The details are as follows.

2.5.6.5.1 Capital Equipment Cost.

The total installed cost of the equipment is $2,770,000. This does not include the cost of the small block valves, which is included in the cost of piping. The cost of each component is listed in Table 37. The total installed cost including piping and design, which are also shown in Table 37, is $4.6 million.

TABLE 37. INSTALLED COST OF MAJOR EQUIPMENT BASED ON 1000 lb OF AGENT PER HOUR

Item	Installed Cost, $
Tanks	1,036,600
Pumps	173,900
Reactors	432,600
Drums	298,600
Coolers	93,500
Heaters	140,400
Columns	447,000
Total Installed Cost	**2,772,600**
25% for Piping + Installation	649,300
25% for Design	811,500
	4,332,300
Cost of Pyrolysis (for GB)	267,400
Total	**4,555,700**
Corresponding cost for a 400 lb/hr agent plant calculated as in the hydrolysis case	2,654,000

2.5.6.5.2 Operating Cost.

Operating cost was also calculated in the same way as for hydrolysis. The details for raw materials and utilities are summarized in Table 38 for each of the three agents.

2.5.6.5.3 Cost of Disposal of By-Products.

By-products waste from nonaqueous chlorinolysis is limited only to GB and VX. All the mustard-by-products are assumed salable to industry. Total waste generated by GB and VX are 401,000 lb and 575,000 lb per site, respectively. Using the same cost analysis as in the hydrolysis process, the total waste disposal cost is estimated to be $226,400/site.

TABLE 38. OVERALL OPERATING COST (excluding labor)*/SITE BASED ON 1600 TONS/SITE TOTAL FOR THE THREE AGENTS

	GB		VX		H	
	lb	$	lb	$	lb	$
Raw Materials						
Chlorine	--	--	169,920[4]	12,320	4,707,840	353,090
Phosgene[1]	678,720	223,980	118,400	39,070	--	--
Sodium Fluoride[2]	288,000	172,800	100,800	60,480	--	--
Carbon Tetrachloride[3]	109,370	26,252	19,120	4,590	192,500	46,200
Ethanol	--	--	38,720	9,990	--	--
Utilities						
Electricity (kW-hr)	21,480	1,070	5,110	260	30,320	1,520
Water	--	--	--	--	--	--
Fuel Oil (gallons)	15,660	18,790	3,950	4,730	23,000	27,600
						1,002,750

[1] Phosgene $.33/lb-0.36/lb (33¢/lb is used)

[2] NaF 60¢/lb

[3] Assuming 1% CCl_4 is lost per pass, and cost is $0.24/lb

[4] Chlorine $145/ton = 7.25 ¢/lb

* Labor = 5 men/shift, 3 shifts/day at $50,000/manyear (0.85 yr) = $637,500
Spare parts = 6% x 4,555,700 x 0.85 = 232,400
Subtotal Operating Cost = 1.873×10^6
Grand Total Operating Cost = 1.874×10^6

2.5.6.5.4 Cost of Thermal Treatment of the Metals and Explosives.

Even though metals and explosives will be washed with solvent such as carbon tetrachloride, they may not be 100 percent agent-free, as described earlier in the hydrolysis section. The total equipment and operation costs for metals and explosives are $2 million and $0.24 million, respectively.

2.5.6.5.5 Total Cost.

The various capital and operations costs for the nonaqueous chlorinolysis process are summarized below:

Nonaqueous chlorinolysis process	
Equipment	$4,600,000
Operation	1,974,000
Cost of by-products disposal	226,000
Cost of metal treatment	0
Cost of explosives incineration	
Equipment	2,000,000
Operation	240,000
Total Cost	$9,940,000

2.5.6.5.6 Value of Products.

The value of the products produced from each agent is summarized in Table 39.

TABLE 39. VALUE OF PRODUCTS PRODUCED FROM EACH AGENT

	Cost/	GB		VX		H	
Material	lb	lb	Cost, $	lb	Cost, $	lb	Cost, $
Cl CH_2 CCl_3	0.45	--	--	--	--	4,051,200	1,863,550
Propylene	0.22	288,000	63,360	--	--	--	--
DF	28.25*	685,440	19,363,680	120,000	3,390,000	--	--
HCl	0.05	554,880	27,740	--	--	3,899,520	194,980
S_2Cl_2	0.15	--	--	--	--	814,080	122,110
Total Value			19,454,780		3,390,000		2,180,640

* From personal communications with Mr. Charles Heyman of Edgewood Arsenal:

- Methylphosphonic dichloride is $17.50/lb.
  (source quotation from Atomergic Chemical Metals Corp.)
- Cost of processing DF from dichloro is at least $5/lb
- Need 1.33 lb dichloro to produce 1 lb of DF (from stoichiometry)
- DF price = ($17.50 x 1.33) + $5.00 = 28.275 (~ $28.25).

2.5.6.5.7 Comparision of Nonaqueous Chlorinolysis with Baseline.

As in the hydrolysis process case, the total cost generated above is based on processing 1000 lb/hour agent. The equipment and operating costs are adjusted for a 400 lb/hr case (same as baseline) using the same assumptions made earlier. The total equipment cost is calculated to be $3.81 million. The operating cost analyses are shown in Table 40.

TABLE 40. ANHYDROUS CHLORINOLYSIS OPERATING COSTS BASED ON 400 lb/hr OPERATION [H:GB:YX 6:3:1, 2.87 Years Operation]

Item	Cost, $	
Raw Material		
Chlorine	365,410	
Phosgene	363,050	
Sodium Fluoride	233,280	
Carbon Tetrachloride	77,040	
Ethanol	9,990	
Utilities		
Electricity	2,850	
Fuel Oil	51,120	
Fixed Cost		
Labor	2,235,000	
Spare Parts	457,100	
Total Chlorinolysis Operating Costs Excluding By-Products Credit		3,794,840
Waste Disposal Cost	226,400	
Explosives Incineration Cost		
Utilities	10,000	
Labor	430,500	
Maintenance	344,400	
Total Plant Operation Costs Excluding By-Products	4,806,140	

Other assumptions are:

(1) The facility which will house the nonaqueous chlorinolysis process is the same size as that which will house the process on which the baseline is based.

(2) The munition disassembly cost will be the same as the corresponding cost for the baseline system.

(3) At this time the same availability of the baseline is assumed for anhydrous chlorinolysis. Results for higher availability are discussed later.

A comparison of the cost of the nonaqueous chlorinolysis process versus the baseline is summarized in Table 41. A total savings of about $48 million per site can be obtained if the anhydrous chlorinolysis process is selected.

2.5.6.5.8 Observations and Conclusions on the Anhydrous Chlorinolysis Process.

The technical and economic analyses performed on the anhydrous chlorinolysis process lead to the following conclusions:

(1) The process is straightforward and uses commercially available and easily scalable equipment. Experiments are required to verify the reaction and develop the kinetics for all the reactions.

(2) The production of the binary agent methyl phosphonic difluoride (DF) is achieved while destroying the agent. DF production is made at a very small capital premium above that of agent destruction.

(3) About $48 million may be saved from each site over the baseline for a total of about $0.5 billion savings on the 10 sites.

(4) The anhydrous chlorinolysis method definitely warrants further investigation in the laboratory because its economic potential is great.

2.5.6.6 Engineering and Economic Evaluation of the Aqueous Chlorination System

Chlorination of the agents is a method which can be used for demilitarization of the three agents. However, it produces large quantities of salts that need proper disposal. Details of the engineering and economic analysis of this method are given below.

TABLE 41. COMPARISON OF THE ANHYDROUS CHLORINOLYSIS PROCESS COSTS (MILLION $) WITH THE BASELINE; BOTH BASED ON 400 lb/hr AGENT

Item	Common Cost	Munition Disassembly Cost	Baseline Process Specific Cost	Anhydrous Chlorinolysis Process Specific Cost*	Total Baseline Cost	Total Anhydrous Chlorinolysis Cost*
Facilities	3.97	1.98	1.43	1.43	7.38	7.38
Equipment	10.44	2.83	21.44	3.81	34.71	17.08
Operation	44.07	4.82	10.26	4.81/(20.22)	59.15	53.70/28.67
Total	58.48	9.63	33.13	10.05/(14.98)	101.24	78.16/53.13

* Operation x/y: x excludes by-product credit
y includes by-product credit

2.5.6.6.1 Kinetics

2.5.6.6.1.1 Kinetics of Hypocchlorination of GB

GB + 10(OCl^-) + NaOH → iso-propylmethyl phosphonate + NaF.

In a study by Epstein et al.,[29] small quantities of chlorine were used to catalyze aqueous caustic hydrolysis of GB. Since the reaction proposed here involves excess hypochlorite (10:1, OCl^- to GB), Epstein's kinetic rates are still usable. The rate constant for the reaction of hypochlorite ion with GB at 25°C was found to be approximately 600 liter per mole per minute. Thus, if we worked in the pH range in which Cl_2 is all in the form of OCl^- (pH ≥ 8.5), we can estimate the half life of GB for any starting concentration of Cl_2. Since Cl_2 acts as a catalyst, the reaction proceeds in a first order decomposition pattern:

$$\frac{\ln A}{A-x} = kt$$

where $k = 600x[OCl^-]$. If $[OCl^-]$ is 1 molar and the pH is maintained at ≥8.5, it can be shown that the half life of GB is less than 0.1 sec.

2.5.6.6.1.2 Kinetics of Acid Chlorinolysis of VX

VX + HOCl → O-ethyl methyl phosphonic acid + N-diisopropyl taurine + HCl

Detoxification of VX by aqueous chlorination under acidic conditions has been extensively studied by Davis.[30] He reports a pseudo first order rate constant (at pH 4 and 25°C) of $k = 6.514 \times 10^2 [Cl^-]\ min^{-1}$. From this k and assuming chlorine is in excess and therefore not rate controlling, the residence time required to reduce the concentration by 10^9 can be calculated, assuming a first order reaction. It is found to be 2.5 sec.

2.5.6.6.1.3 Kinetics of Acid Chlorinolysis of H

$$H + 14\ HOCl \xrightarrow{\text{Slightly acidic condition}} H_2SO_4 + 16HCl + 4CO_2 + 2H_2O$$

Detoxification of H to these products is a complex reaction involving a number of steps. No literature information was found giving rate constants on the reaction sequence. The initial reaction, however, is expected to be almost instantaneous after the mustard has been dissolved in the aqueous media (a mixture of water and acetone) (see kinetics of water hydrolysis of H). However, the final sequence of reactions producing the sulfuric and hydrochloric acid and carbon dioxide may not be as rapid. An excess of chlorine is necessary to improve the rates of reaction.

The overall reaction is expected to be on the order of minutes. Experimental data will be needed to substantiate this expectation.

2.5.6.6.2 Process Description

Figure 13 is a process flow diagram for the aqueous chlorination of the three agents. Also incorporated in this diagram is a chlor-alkali electrolysis cell to generate the chlorine on site and thereby decompose the salts which otherwise would require disposal. The analysis is performed with and without a chlorine plant on site.

In general, the agent is mixed with chlorinated water which is produced on site by bubbling chlorine through water in reactor T-102. HCl or NaOH is also added, depending on which agent is being processed, to control the pH. In the case of mustard, a solvent is also added since mustard is not soluble in chlorinated water. The mixture goes through a static mixer and from there to reactor T-103 which is also equipped with a stirrer. This reactor provides the required residence time for the reaction. Because of the uncertainty in the kinetics of this process, this reactor was designed to provide up to 1 hour of residence time. The pH of the products leaving the reactor is adjusted and their separation begins. The configuration of Figure 13 and its details for each agent are discussed below.

2.5.6.6.2.1 Hypochlorination of GB

- GB + HOCl + NaOH → Na-isopropyl methyl phosphonate + NaF + NaCl

  Na-iPr methyl phosphonate + HCl $\xrightarrow{\Delta}$ iPrOH + NaF + MPA + NaCl

  MPA + NaF + lime → Calcium salt of MPA + CaF

  $2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$

- GB is soluble in water.

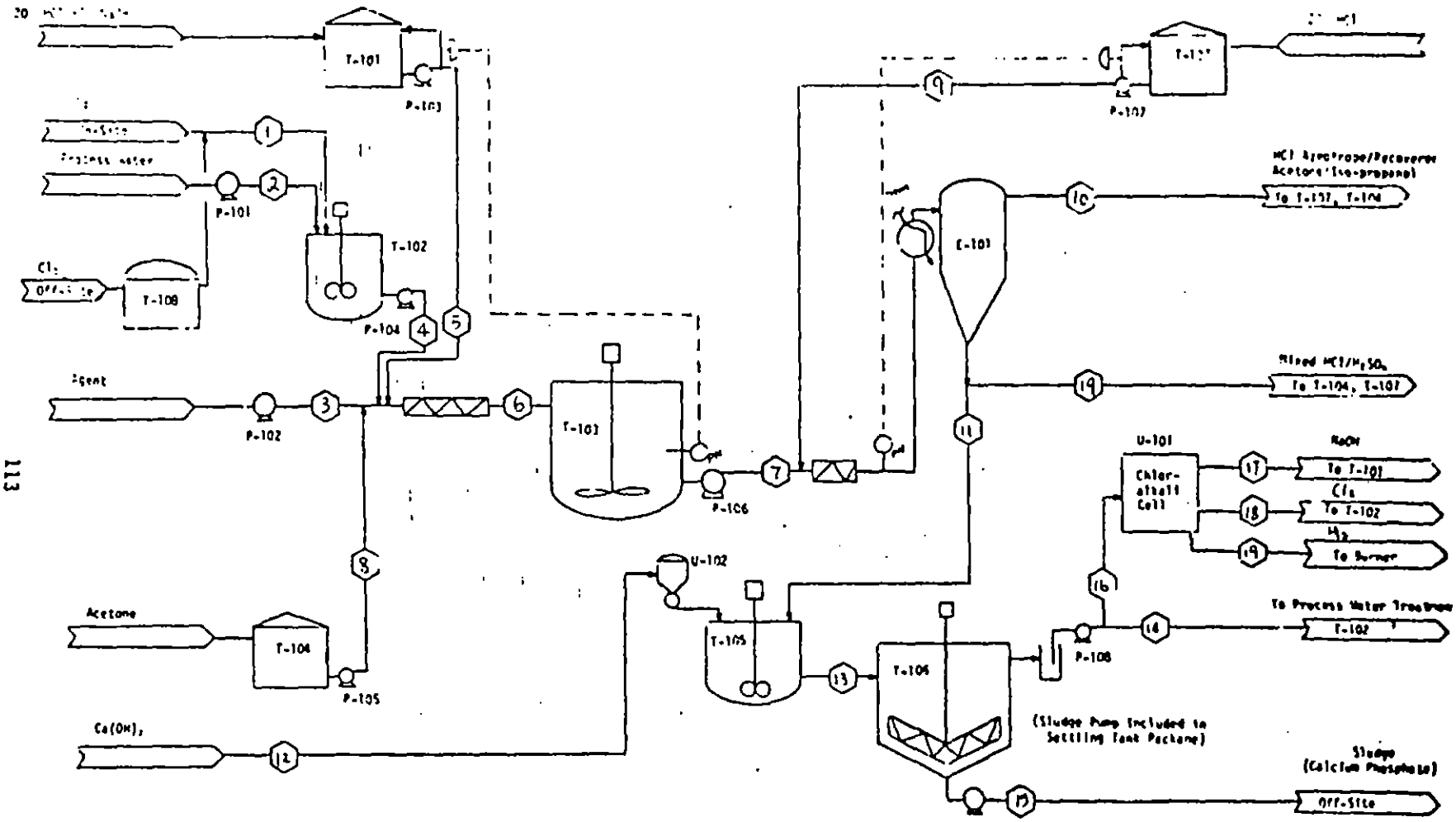


Figure 13. Process flow diagram for the aqueous chlorination of [illegible]

- Isopropanol (82 percent) is produced and could be sold.
- MPA and calcium fluoride are final products and could be sold for the manufacture of elemental phosphorus. MPA could also be used to manufacture DF.
- A 25 percent NaCl brine stream is produced which could be used for the generation of chlorine in an electrolytic cell, or could be disposed of by landfilling. The large amounts of brine produced makes this expensive.

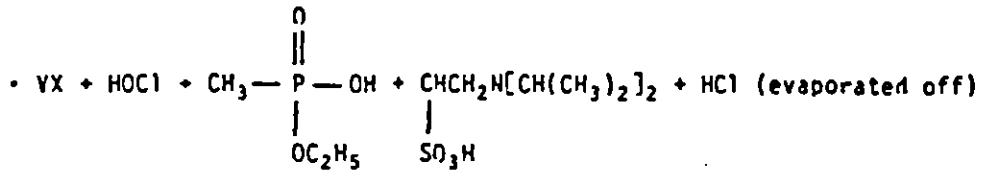
Process Description. The reaction takes place under alkaline conditions, pH 8-9. A caustic solution is added in-line before the static mixture. The caustic feed is controlled by a pH controller based on a pH probe in chlorination reactor T-103. The products from T-103 include sodium isopropyl methyl phosphonate, sodium fluoride, and sodium chloride. The pH of this mixture is adjusted with hydrochloric acid to around 1-2 to facilitate breaking of the isopropyl group. The mixture is then raised to its boiling point and isopropanol is removed as an azeotrope from the top of evaporator E-101.

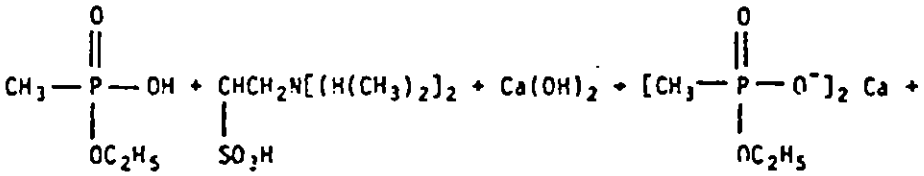
The acid addition and displacement of the isopropyl group creates more sodium chloride. The resulting brine stream from the evaporator bottoms contains sodium salts of methyl phosphonic acid and sodium fluoride. These are reacted with lime to precipitate out the highly insoluble calcium fluoride and calcium salt of MPA. This stream is separated out in clarifier T-106. The supernatant is a brine stream consisting of approximately 25 percent sodium chloride.

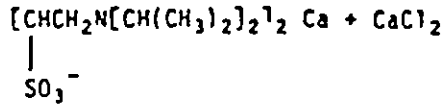
The calcium salts could be sold to a manufacturer of elemental phosphorus. The brine stream could be used for the generation of chlorine in an electrolytic cell. If the chlorine electrolytic cell is not purchased, the salts could be evaporated to a dry cake and landfilled. The brine could be dried through pond evaporation for sites in the western part of the country and thus reduce the operating costs significantly. Since the NaCl produced has gone through several processing stages it is very unlikely to contain residual GB.

Note that if a chlor-alkali cell is installed on site it completely solves the disposal problem since no other products from G3 require disposal. NaCl will have to be brought to the site in order to generate enough Cl_2 for the chlorinolysis process.

2.5.6.6.2.2 Acid Chlorinolysis of VX







- VX is slightly soluble in water, but more soluble in acidic conditions. Therefore there is no need to add solvent to the chlorinated water.
- Hydrochloric acid is produced in the reaction and removed at a concentration of around 88 percent. Therefore it could be sold.
- Calcium phosphonate is produced and could be sold for the production of elemental phosphorus.

Process Description. Chlorination of VX takes place at acidic conditions, pH 3-4. Hydrochloric acid is added to the influent agent-chlorine solution at a rate set by a pH controller in chlorination reaction tank T-103. The product of acid chlorination is an acidic solution which contains O-ethyl methyl phosphonic acid and diisopropyl taurine. Some of the acid is removed by evaporation in evaporator E-101. The hydrochloric acid is removed as an azeotrope with water (approximately 20 percent hydrochloric acid). The bottoms from the evaporator are reacted with lime to precipitate out the calcium salts of the o-ethyl methyl phosphonic acid. The salt is highly insoluble in water and can be separated in clarifier T-106.

The salt could be sold for the manufacture of elemental phosphorus. The supernatant contains a high concentration of calcium chloride, but only a small volume is produced and thus could be blended in with the process water and reused without further treatment. Chlorination of VX, therefore, does not

produce any waste products which require disposal, except the taurine solids which are easy to dispose of.

2.5.6.6.2.3 Acid Chlorinolysis of H

- Mustard + 14 HOCl ⟶ H_2SO_4 + 16HCl + $4CO_2$ + H_2O
- Mustard is insoluble in water, but its high reactivity makes it more soluble in chlorinated water
- A mixed acid is produced that is approximately 20 percent hydrochloric and 2 percent sulfuric acid. This acid can be recycled and reused within the process, the excess sold as a slightly contaminated hydrochloric acid.

Process Description. The chlorination of mustard takes place under slightly acidic conditions, which promote the solubility of the mustard and therefore improve the overall reaction rate. Acetone is also added to solubilize the mustard since this will be the determining step. The overall reaction is shown above although chlorination of H to these products takes place in a number of steps.

The chlorinated water and acetone are added to the mustard and hydrochloric acid is added in line prior to a static mixer. The agent solution is then discharged to a reactor. A pH probe in this reactor provides feedback to a control valve in the acid feed system. The pH is maintained in the range of 1-2. Up to 60 minutes of reaction time is allowed to ensure complete reaction to the products above. The reacted products are fed to an evaporator where the acetone is recovered. The acetone is removed as an azeotropic mixture with water that is approximately 88 percent acetone. The remaining water from the evaporator bottoms is an acidic mixture, approximately 20 percent hydrochloric and 2 percent sulfuric acid. This acid can be stored in either T-101 or T-107 and sold. Some of it can be used on-site for pH control.

Chlorinolysis of H does not produce any waste products that need disposal. Of the three agents, only GB produces NaCl, which will need disposal if not electrolyzed to reproduce Cl_2 and NaOH.

2.5.6.6.3 Material and Energy Balances

Material and energy analyses were performed on the three configurations of Figure 13 as they apply to the chlorinolysis of 1000 lb of agent per hour for each of the three agents. The results from the material balance analysis

are summarized in Tables 42, 43, and 44 for GB, VX, and H respectively. The energy requirement of the system, excluding the drying of the salt produced from GB which is calculated separately, is negligible and thus was calculated only to estimate the size of the pumps.

2.5.6.6.4 Design Criteria of the Aqueous Chlorinolysis System

Table 45 summarizes the design criteria for the major components of the system.

2.5.6.6.5 Economic Evaluation

The economic evaluation procedure adopted for this process is similar to that used for water hydrolysis. Two additional sources were used for costing the hardware: U.S. EPA Treatability Manual, Vol. IV, "Cost Estimating," 1980, and Power Magazine, July 1974.

All figures were updated to 1982 dollars with the CE Plant Cost Index. The equipment sizes were determined using the worst case, or highest flow rate conditions of the three agents.

Two alternatives were costed with and without the purchase of an on-site chlorine generator. The advantages of the purchase of an on-site chlorine generator would be operational, since chlorine would not have to be delivered to the facility and personnel handling of the chlorine would be less with an on-site chlorine generator.

The other advantage of on-site chlorine generation is the elimination of the by-product sodium chloride brine generated from GB processing. If this brine is not used for chlorine generation, it will have to be disposed of. The disposal method for brine is energy intensive because it requires heat drying followed by disposal in a sanitary landfill. This assumes that the local landfill operator will accept the sodium chloride solids for disposal. Since the waste should be all sodium chloride, there should be no objection to its landfill in this manner, however, the origination of the salts in a CW decontamination may be a cause for concern.

The disadvantage of the on-site chlorine generator is economical, since the process, sized to deliver chlorine for the worst case (i.e., H), would cost about $10,000,000. Since the generator itself is not in direct contact

TABLE 42. MATERIAL BALANCE CALCULATIONS FOR HYPOCHLORINATION OF GB

Stream / Compound lb/hr	1 Chlorine Gas	2 Process Water	3 GB	4 Chlorine Solution	5 50 % NaOH	6 Reactor Feed	7 Hypo Chlorination Products	9 20% HCl Solution	10 Isopropanol Water Mixture	11 Brine Mixture	12 Lime Addition	13 Brine and Lime	15 Calcium Salts to Disposer	16 NaCl Brine	17 Cl_2	18 NaOH	19 H_2
Cl_2	5057														5079		
GB			1000			1000											
HOCl				3714		3714											
Water		20230		18944	2857	21801	24282	2501	59	26440		26648	4796	21852		20556	
NaOH					2857	2857										2857	
Sodium Isopropyl Methyl Phosphonite							971			3379		3379		3379			
NaF							300			300							
NaCl							3314			3729		4143		4143			
Cl^-				2629		2629	3129			3379		3379		3379			
HCl								514									
MPA										696							
IPrOH									429								
$Ca(OH)_2$											793						
Ca-MPA												736	736				
H_2																	82
TOTAL	5057	20230	1000	25287	5714	32001	32001	3021	488	37913	793	38284	5532	32753	5079	23413	82

TABLE 43. MATERIAL BALANCE CALCULATIONS FOR ACID CHLORINOLYSIS OF YE

Compound lb/hr \ Stream	1 Chlorine Gas	2 Process Water	3 YE	4 Chlorine Solution	5 20% HCl Solution	6 Reactor Feed	7 Chlorination Products	10 HCl Azeotrope	11 Boiler Bottoms	12 Lime Feed	13 Neutralized Mixture	14 Recovered Water	15 Calcium Salts to Landfill
Cl_2	2,883												
YE			1,000			1,000							
HOCl				2,389		2,389							
HCl				1,235	378	1,613	3,017	2,378	639				
Water		11,532		10,791	1,890	12,681	13,419	9,393	4,026		5,142	3,599	1,543
$CH_3-P(=O)(OC_2H_5)-OH$							464		464				
$CH_2CH_2N[CH(CH_3)_2]_2$ | SO_3H							783		783				
$Ca(OH)_2$										1591			
$[CH_3-P(=O)(OC_2H_5)-O^-]_2Ca$											535		535
$CaCl_2$											476	967	
$[CH_2CH_2N[CH(CH_3)_2]_2$ | $SO_3^-]_2Ca$											850		850
Total	2,883	11,532	1,000	14,415	2,268	17,683	17,683	21,164	9,938	1,591	12,645	8,165	4,471

TABLE 44. MATERIAL BALANCE CALCULATIONS FOR ACID CHLORINOLYSIS OF H

Stream / Compound lb/hr	1 Chlorine Gas	2 Process Water	3 H	4 Chlorine Solution	5 20% HCl Solution	6 Reactor Feed	7 Hypochlorination Products	8 Acetone Feed	10 Recycled Acetone	19 Mixed Acid
Cl_2	6202									
H			1000			1000				
H_2O		24808		23214	3328	26542	26770		322	26448
Acetone						2481	2481	2481	2481	
HOCl				4607		4607				
HCl				3189	832	4021	7666			7666
H_2SO_4							620			620
CO_2							1114		1114	
TOTAL	6202	24808	1000	31010	4160	38651	38651	2481	3917	34734

TABLE 45. MAJOR EQUIPMENT REQUIREMENTS FOR AQUEOUS CHLORINATION PROCESS AT 1000 lb/hr WITH CHLORINE GENERATOR

Equipment	Design Criteria and Size
Tanks	
T-101 Acid/caustic storage (stainless steel)	240,000 gal
T-102 Chlorine reactor	760 gal
T-103 Chlorination tank	6,400 gal (sized to provide up to 60 min residence time)
T-104 Acetone storage (stainless steel)	203,000 gal
T-105 Lime mix tank	750 gal
T-106 Clarifier	Sized for 4 hour retention time with 1.2 excess capacity, includes 2 carbon steel tanks, 2 sludge pumps, and sludge skimmer.
T-107 Acid storage (stainless steel)	106,000 gal
Pumps	
P-101 Process water	65 gpm, 0.25 HP
P-102 Agent solution	105 gpm, 1 HP
P-103 Acid/caustic	10 gpm, 0.25 HP
P-104 Chlorine solution	85 gpm, 0.25 HP
P-105 Acetone	10 gpm, 0.25 HP
P-106 Product	105 gpm, 2 HP
P-107 Acid	7 gpm, 0.25 HP
P-108 Brine	45 gpm, 0.25 HP
Other Equipment	
E-101 Evaporator--horizontal tube	300 ft^2
U-101 Chlorine/caustic electrolytic cell	27 units each with 5,600 lb/day capacity (sized to generate chlorine for worst case, i.e., H at 6,200 lb/hr)
Cyclone lime collector	2,000 cfm
Hopper	9,550 cubic feet
Screw feeder	6 in. auger dia., 2 ft length

with the CW agents, it could possibly be sold at the end of the decontamination of all of the agents for a good percentage of its initial investment. However, no resale credit of this unit is assumed in our analysis.

Details of the installed cost, operating cost, total costs, and comparison with the R&D baseline follows.

2.5.6.6.5.1 Capital Equipment Cost

The installed costs of the major components listed in Table 45 are summarized in Table 46 for the case including the electrolysis cell. The corresponding total capital investment, calculated in Table 47, shows a total installed cost of $17,253,000.

The same analyses were made for the case of no on-site generation of Cl_2. The results, summarized in Tables 48 and 49, show a total of $1,789,000.

In both cases the capital investment is fairly high. It is very high in the case where Cl_2 will be generated on site.

2.5.6.6.5.2 Operating Costs

Operating costs were determined from the material balances. Baseline fuel, electricity, and water unit prices were used. Chemical costs were taken from the Chemical Marketing Reporter (September 13, 1982).

Operating costs were developed for cases with and without a chlorine generator. With the chlorine generator, the major differences in the operating costs are from the cost credits from the generation versus the purchase of chlorine, the generation and sale of sodium hydroxide from the chlorine generation, and the generation and use for fuel of hydrogen produced in the chlorine generation. Power costs, however, are high for chlorine generation, 3 kWhr/lb of chlorine.

The operating costs, excluding labor and spare parts for the case with on-site generation of Cl_2, are summarized in Tables 50, 51, and 52. The actual cost from Table 17 is about $156,000 for chemicals and $871,700 for utilities or a total of $1,027,800. Additional credits which may be obtained from GB with on-site generation are summarized in Table 53. A total credit for products that will not be used internally totals about $139,400.

In the case of VX, Table 51 shows a total operating cost, excluding labor and spare parts, of $246,530. Table 54 shows a total net credit of $228,400.

TABLE 46. INSTALLED EQUIPMENT COSTS FOR AQUEOUS CHLORINATION PROCESS AT 1,000 lb/hr WITH CHLORINE GENERATOR

Equipment	Installed Cost, 1982 ($)
Tanks	
T-101	293,000
T-102	17,000
T-103	47,000
T-104	275,000
T-105	16,000
T-106	84,000
T-107	166,000
Pumps	
P-101	2,300
P-102	5,300
P-103	4,000
P-104	3,400
P-105	4,000
P-106	4,300
P-107	4,000
P-108	4,200
Mixers	
Static (2)	10,000
Propeller (3)	1,500
Other Equipment	
pH Controllers (2)	10,000
Chlor/alkali electrolytic cell	10,000,000*
Lime storage and feeder	43,000**
Evaporator	48,000
Total Equipment Installed Cost	11,042,000

* Maximim Cl_2 needed to decontaminate 1,000 lb of agent (H) is 6,200 lb/hr. Since a large electrolytic cell can produce 5,600 lb/day of Cl_2, we need 27 of these units. Installed cost of each unit in 1974 is quoted by Power Magazine to be $237,500; total cost in 1982 is $237,500 x 27 x 1.6.

** Costed as three parts: cyclone collector = $16,000, bin or hopper = $24,000, and screw conveyor feeder = $3,000.

TABLE 47. TOTAL CAPITAL INVESTMENT FOR AQUEOUS CHLORINATION PROCESS FOR GB, VX, AND H AT 1,000 lb/hr WITH CHLORINE GENERATOR

Item	Installed Cost, 1982 ($)
Total Installed Cost	11,042,000
Piping (25% of TIC)	2,760,500
Total Capital Investment (no contingency)	13,802,500
Design (25% of TIC)	3,450,625
Total Installed Cost of Chlorination Plant (including Chlorine Generator Plant)	17,253,125

TABLE 48. INSTALLED EQUIPMENT COSTS FOR AQUEOUS CHLORINATION PROCESS AT 1,000 lb/hr WITHOUT CHLORINE GENERATOR

Equipment	Installed Cost, 1982 ($)
Tanks	
T-101	293,000
T-102	17,000
T-103	47,000
T-104	275,000
T-105	16,000
T-106	84,000
T-107	166,000
T-108	103,000
Pumps	
P-101	2,300
P-102	5,300
P-103	4,000
P-104	3,400
P-105	4,000
P-106	4,300
P-107	4,000
P-108	4,200
Mixers	
Static (2)	10,000
Propeller (3)	1,500
Other Equipment	
pH Controllers (2)	10,000
Lime storage and feeder	43,000
Evaporator	48,000
Total Equipment Installed Cost	1,145,000

TABLE 49. TOTAL CAPITAL INVESTMENT FOR AQUEOUS CHLORINATION PROCESS AT 1,000 lb/hr WITHOUT CHLORINE GENERATOR

Item	Installed Cost, 1982 ($)
Tanks and Clarifier	1,001,000
Pumps	31,500
Mixers (2 in-line static, 3 propeller)	11,500
Instrumentation (2 pH controllers)	10,000
Special equipment	
Lime storage and feeder	43,000
Evaporator	48,000
Total Installed Cost	**1,145,000**
Piping (25% of TIC)	286,250
Total Capital Investment (no contingency)	**1,431,250**
Design (25% of TIC)	357,800
Total Installed Cost of Chlorination Plant	**1,789,050**

TABLE 50. BREAKDOWN OF OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF GB AT 1,000 lb/hr FOR 480 TONS OF GB* WITH CHLORINE GENERATOR

Item	lb/lb Agent	Consumption	Unit Cost, $	Total Cost, $
Chemical				
Sodium hydroxide	5.714	110 tons	285/ton	31,350
Hydrochloric acid (20%)	3.021	1,500 tons	34/ton	51,000
Calcium hydroxide	0.793	500 tons	32.50/ton	16,250
NaCl as feed stock to Cl_2 generator--over what is produced in house		1,150 tons	50/ton	57,500
Utilities				
Electricity for process		8,400 kWhr	0.05/kWhr	400
Electricity for Cl_2 generation		17,000,000 kWhr	0.05/kWhr	870,000
Water	20.23	$2,400/ 1,000 gal	0.53/ 1,000 gal	1,300
Subtotal				871,700
Total Operating Cost for A+B				1,027,800

* GB is assumed to constitute 30% of the total amount of agents at each site (0.3 x 1600 = 480)

TABLE 51. BREAKDOWN OF OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF VX AT 1,000 lb/hr FOR 160 TONS OF VX* WITH CHLORINE GENERATOR

Item	lb/lb Agent	Consumption	Unit Cost, $	Total Cost, $
Chemicals				
Calcium hydroxide	1.6	307 tons	32.50/ton	10,000
NaCl for electrolysis process		920 tons	50/ton	46,000
Subtotal				56,000
Utilities				
Electricity for process		2,800 kW/hr	0.05/kWhr	140
Electricity for Cl_2/NaOH plant		3,342,000 kW/hr	0.05/kWhr	167,100
Water	11.5	441,000 gal	0.53/1,000 gal	250
Fuel oil	0.093 gal/lb agent	19,200 gal	1.2/gal	23,040
Subtotal				190,530
Total Operating Cost for A+B				246,530

* VX is assumed to constitute 10% of the total amount of agents at each site (0.10 x 1600 = 160).

TABLE 52. BREAKDOWN OF OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF H AT 1,000 lb/hr FOR 960 TONS OF H* WITH CHLORINE GENERATOR

Item	lb/lb Agent Consumption		Unit Cost, $	Total Cost, $
Chemicals (+20%)				
Acetone	2.5	576 tons	620/ton	357,120
NaCl for electrolysis plant		11,700 tons	50/ton	585,000
Subtotal				942,120
Utilities				
Electricity for process		17,000 kWhr	0.05/kWhr	850
Electricity for electrolysis		42,900,000 kWhr	0.05/kWhr	2,145,000
Water	25	5,800 1,000 gal	0.53/ 1,000 gal	3,000
Subtotal				2,148,850
Total Operating Cost				3,090,970

* H is assumed to constitute 60% of the total amount of agents at each site (0.60 x 1600 = 960).

TABLE 53. CREDITS FROM GB WITH ON-SITE GENERATION OF Cl_2

Product	Cost, $
Isopropanol (88%)	110,600
0.48 lb isopropanol produced/lb agent decontaminated, at $0.24/lb value, 460,800 lb produced	
Calcium phosphonate/calcium fluoride solids	28,800
Sold for production of elemental phosphorus, assumed value = $10/ton, 6 lb solids produced/lb agent decontaminated, 2,800 tons	
Total Net Credit	139,400

TABLE 54. CREDITS FROM VX WITH ON-SITE GENERATION OF Cl_2

Product	Cost, $
Hydrochloric acid (20%) Generated in decontamination process, 1,883 tons generated at $34/ton, 442 tons will be used on-site value of net to be sold	49,000
Calcium phosphonate/calcium taurine salts Sold for production of elemental phosphorus, assume $10/ton value, 470 tons produced	4,700
NaOH Generated with the chlorine, 1.1 lb NaOH/lb chlorine generated, 613 tons generated at $285/ton	174,700
Total Net Credit	**228,400**

Other fixed costs were also calculated. Spare part costs were taken as 5 percent of capital investment per year. Labor requirements were estimated at 7 men per shift, 3 shifts a day. The results are summarized in Table 56. This table also shows the total cost (capital and operating for the plant with and without credit).

Similar analyses were done for the case without on-site generation of chlorine. The results are summarized in Tables 57 through 63.

TABLE 55. CREDITS FROM H WITH ON-SITE GENERATION

Product	Cost, $
HCl Excess of 28,742 tons sold, since it contains 2% sulfuric acid, use value of $30/ton	854,160
NaOH Generated with the chlorine, 1.1 lb NaOH/lb chlorine generated, 7,865 tons generated, at 285/ton	2,241,525
Total Net Credit	**3,095,585**

TABLE 56. COST SUMMARY FOR AQUEOUS CHLORINATION OF GB, VX, AND H AT 1,000 lb/hr WITH ON-SITE CHLORINE GENERATION

Item	Cost Without Credit, 1982 ($)
Total Installed Equipment Cost	17,253,125
Operating Costs	
Chemicals and utilities	4,365,300
Spare parts cost at 6% of capital investment/yr (0.85 yr)	703,930
Labor, 7 men/shift, $50,000/yr, (0.85 yr), 3 shifts	892,500
Overall Cost	23,214,800
Total Net Credit	3,463,485
Overall Cost with Credit	19,751,300

TABLE 57. OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF GB AT 1,000 lb/hr FOR 480. TONS OF GB WITHOUT CHLORINE GENERATOR

Item	lb/lb Agent	Consumption	Unit Cost, $	Total Cost, $
Chemicals				
Chlorine	5.057	2,900 tons	145/ton	420,500
Sodium hydroxide (50%)	5.714	3,300 tons	285/ton	940,500
Hydrochloric acid (20%)	3.021	1,500 tons	34/ton	51,000
Calcium hydroxide	0.793	500 tons	32.50/ton	16,250
Total				**1,428,250**
Utilities				
Electricity		8,400	0.05/kWhr	400
Water	20.23	$ 2,400/ 1,000 gal	0.53/ 1,000 gal	1,300
Fuel oil (0.038 gal/lb agent)		36,480	1.20/gal	44,000
Total				**45,700**
Waste Handling				
25% sodium chloride brine produced, if given to a waste hauler for evaporation and sanitary landfill assume: $190/ton for heat drying,* at $0.05/100 miles transportation (1,500 miles)/gal $83/ton for land disposal,* 29.3 lb of brine/lb agent detoxified, or 3 gal/lb agent (1.1 sp. gr.) 14,064 tons or 3 million gal $2,672,000 (heat drying) + $2,250,000 (transport) + $1,170,000 (landfill)				6,092,000
Total Operating Cost				**7,565,950**

* Reference: Rimkus, R., et al. "Solids Handling Systems for Six Different Disposal Operations," J. WPCF, 52, (4), April, 1980.

TABLE 58. OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF VX AT 1,000 lb/hr FOR 160 TONS OF VX, WITHOUT CHLORINE GENERATOR

Item	lb/lb Agent	Consumption	Unit Cost, $	Total Cost, $
Chemicals				
Chlorine	2.9	557 tons	145/ton	80,800
Hydrochloric acid	2.3	442 tons	34/ton	15,000
Calcium hydroxide	1.6	307 tons	32.50/ton	10,000
Subtotal				105,800
Utilities				
Electricity		2,800 kWhr	0.05/kWhr	140
Water	11.5	441,000 gal	0.53/1,000 gal	250
Fuel oil	0.093 gal/lb agent	30,000 gal	1.2/gal	36,000
Subtotal				36,390
Total				142,190

TABLE 59. OPERATING COSTS AND CREDITS FOR THE AQUEOUS CHLORINATION OF H AT 1,000 lb/hr FOR 960 TONS OF H WITHOUT CHLORINE GENERATOR

Item	lb/lb Agent	Consumption	Unit Cost, $	Total Cost $
Chemical				
Chlorine	6.2	7,150 tons	145/ton	1,037,000
Acetone	2.5	576 tons*	620/ton	357,200
Subtotal				1,394,200
Utilities				
Electricity		17,000 kWhr	0.05/kWhr	850
Water	25	558,000/ 1,000 gal	0.53/ 1,000 gal	3,000
Fuel oil	0.036 gal/ lb agent	69,000	1.20/gal	83,000
Subtotal				86,850
Operating Cost, A+B				1,481,050

* Assuming 80% recovery of acetone

TABLE 60. CREDITS FROM GB WITHOUT ON-SITE GENERATION OF Cl_2

Product	Cost, $
Isopropanol (88%) Generated on-site 0.48 lb/lb agent, 461,000 lb produced at $0.24/lb	110,600
Calcium phosphonate/calcium fluoride solids Sold for production of elemental phosphorus, assume $10/ton value, 6 lb calcium salt (including water)/lb agent detoxified 2,800 tons produced	28,800
Total Net Credit	139,400

TABLE 61. CREDITS FROM VX WITHOUT ON-SITE GENERATION OF Cl_2

Product	Cost, $
Hydrochloric acid (20%) 1,883 tons generated, 442 used on-site, net for sale 1,441 ton at $34/ton	49,000
Calcium phosphonate/calcium taurine solids Sold for production of elemental phosphorus, assume $10/ton value, 470 tons produced	4,700
Total Net Credit	53,700

TABLE 62. CREDITS FROM H WITHOUT ON-SITE GENERATION OF Cl_2

Product	Cost, $
Excess HCl/H_2SO_4 28,472 tons at $30/ton	854,160

TABLE 63. COST SUMMARY FOR AQUEOUS CHLORINATION OF GB, VX, AND H AT 1,000 lb/hr WITHOUT CHLORINE GENERATOR

Item	Cost With Credit, 1982 ($)
Total installed equipment cost	1,789,050
Operating costs	
Chemicals and utilities	9,189,200
Spare parts at 6% of capital investment/yr (0.85 yr)	73,000
Labor, 5 men/shift, 3 shifts, $50,000 ann. (0.85 yr)	637,500
Overall Cost	**11,688,700**
Total Net Credit	**1,047,260**
Overall Cost with Credit	**10,641,400**

2.5.6.6.5.3 Total Costs

Costs obtained in different sections and the cost of thermal treatment of the explosives and the metals as described in the discussion on the hydrolysis method are summarized here to come up with the total cost. The results are shown in Table 64.

TABLE 64. TOTAL COST OF AQUEOUS CHLORINATION OF AGENTS

Item	With On-Site Generation of Cl_2		Without On-Site Generation of Cl_2	
	W/O Credit	With Credit	W/O Credit	With Credit
Total Equipment and Operation Costs	$23,214,800	$19,751,300	$11,688,700	$10,641,400
Metals and Explosives	$ 2,250,000	$ 2,250,000	$ 2,250,000	$ 2,250,000
Total Cost for Demilitarizing the Three Agents	$25,464,900	$22,001,300	$13,938,700	$12,891,400

2.5.6.6.5.4 Comparison With Baseline

The procedure is similar to that followed for the hydrolysis process. The economic analysis for aqueous chlorination was done on the basis of 1000 lb/hr of agent processed. The systems were therefore scaled down to 400 lb/hr

of agent. The equipment costs were adjusted similarly to the method used for hydrolysis.

Operating costs were estimated somewhat differently. Operating costs for aqueous chlorination with and without an on-site chlorine generator are broken down in Tables 65 and 67, respectively. Comparisons of equipment and operating costs for the 400 lb/hr cases with and without the on-site chlorine generator are given in Tables 66 and 68, respectively. In both cases, the total chemical process cost is less than the baseline.

The case with the on-site chlorine generator has a higher capital but lower operating cost than the case without the chlorine generator. The lower operating cost with the chlorine generator is a result of purchasing the lower cost sodium chloride for chlorine generation over the higher cost chlorine, recycling the hydrogen produced with chlorine generation for heat recovery, and using caustic generated with the chlorine generation for pH adjustment in GB decontamination. The higher credits with the chlorine generator are primarily a result of the sale of the excess sodium hydroxide produced.

TABLE 65. OPERATING COSTS FOR AQUEOUS CHLORINATION H:GB:VX, 6:3:1 (YEAR OPERATION) WITH CHLORINE GENERATOR (SAME SYSTEM AVAILABILITY AS BASELINE) [Based on 400 lb/hr Operation]

Item	Cost, $
Chemicals and utilities	4,365,300
Spare parts at 6% of capital investment/yr (2.87 yr)	2,376,800
Labor, 7 men/shift, $50,000 ann. (2.87 yr)	3,013,5000
Total Operating Cost Excluding Credits	9,755,600

TABLE 66. COMPARISON OF THE AQUEOUS CHLORINATION PROCESS WITH CHLORINE GENERATOR WITH THE BASELINE
[Both Based on 400 lb of Agent per Hour]

Item	Common Cost, $	Munition Disassembly Cost, $	Baseline Process-Specific Cost, $	Aqueous Chlorination Process-Specific Cost, $*	Total Baseline Cost, $	Total Chemical Process Cost, $*
Facilities	3.97	1.98	1.43	1.43	7.38	7.38
Equipment	10.44	2.83	21.44	11.11**	34.71	24.38
Operation	44.07	4.82	10.26	10.68/ 7.22***	59.15	59.57/ 56.11
Total	58.48	9.63	33.13	23.22/ 19.76	101.24	91.33/ 87.87

* Operation x/y x excluding by-products credit; y including by-products credit; size plant scale-up is based on 0.6 power.

** Cost for 400 lb/hr plant = $(17.253 + 2.0) \times 10^6 (400/1000)^{0.6} = 11.11$

*** Operating cost for 400 lb/hr plant

Aqueous chlorination process	= 9.76×10^6
Incinerator labor: 3 men x $50,000 x 2.87 yr	= 0.431×10^6
Utilities	= 0.020×10^6
Maintenance: 6% x 2.87 yr x 2.0×10^6	= 0.344×10^6
Total	= 0.785×10^6
Disposal	= 0.134×10^6
Grand Total	= $10.679
Credit	= 3.463×10^6

TABLE 67. OPERATING COSTS FOR AQUEOUS CHLORINATION H:GB:VX 6:3:1 (YEAR OPERATION) WITHOUT CHLORINE GENERATOR (SAME SYSTEM AVAILABILITY AS BASELINE)
[Based on 400 lb of Agent per Hour]

Item	Cost, $
Chemicals and utilities	9,189,200
Spare parts at 6% of capital investment/yr (2.87 yr)	142,800
Labor, 7 men/shift, 3 shifts, $50,000 ann. (2.87 yr)	2,152,500
Total Operating Cost, Excluding By-Product	11,483,700

TABLE 68. COMPARISON OF THE AQUEOUS CHLORINATION PROCESS WITHOUT CHLORINE GENERATOR WITH THE BASELINE
[Based on 400 lb of Agent per Hour]

Item	Common Cost, $	Munition Disassembly Cost, $	Baseline Process-Specific Cost, $	Aqueous Chlorination Process-Specific Cost, $*	Total Baseline Cost, $	Total Chemical Process Cost, $*
Facilities	3.97	1.98	1.43	1.43	7.38	7.38
Equipment	10.44	2.83	21.44	2.19**	34.71	15.46
Operation	44.07	4.82	10.26	12.4/11.35***	59.15	61.29 60.24
Total	58.48	9.63	33.13	16.02/14.97	101.24	84.13/83.08

* Operation x/y x excluding by-products credit; y including by-products credit; size plant scale-up is based on 0.6 power.

** Cost for 400 lb/hr plant = $(1.79 + 2.0) \times 10^6 (400/1000)^{0.6} = 2.19$

*** Operating cost for 400 lb/hr plant

Aqueous chlorination process = 11.48		
Incinerator labor: 3 men x $50,000 x 2.87 yr	=	$0.431 x 10^6
Utilities	=	0.010 x 10^6
Maintenance: 6% x 2.87 yr x 2.0 x 10^6	=	0.344 x 10^6
Total	=	$0.785 x 10^6
Disposal	=	0.134
Credit (Table 63)	=	1.047 x 10^6
Grand Total	=	$12.4 x 10^6

2.5.6.6.5.5 Conclusions

The preceding engineering evaluation of the aqueous chlorination process yields the following conclusions:

(1) The process is reasonably straightforward and can take place in conventional scalable equipment. Although one reaction takes place under alkaline conditions and the other two at acid conditions, the same equipment can be used interchangeably. The kinetics of the acid chlorinolysis of VX has been well studied, but the reaction rates of GB and H to the desired products require further study.

(2) Purchase of an on-site chlorine generator will completely solve the waste disposal problem. Calcium sludges produced in GB and VX decontamination can be sold for elemental phosphorus production. However, a large quantity of 20 percent sodium cloride brine is produced in GB decontamination. No salts are formed in the H decontamination. If the sodium chloride brine is used in the generation of chlorine in an electrolytic cell, there are no disposal problems. If there is no electrolytic cell, the alternative is to heat dry the brine to a cake and landfill the cake. This is an expensive alternative. An alternative to the heat drying is lagooning and evaporation. This assumes that a good deal of land is available for a large retention time of the brine, and that the net precipitation in the area is negative (that is, more water is evaporated than precipitated). Another advantage of the on-site chlorine generator is safety. The case without the generator assumes delivery of chlorine every other day. This means that the chlorine has to be transported to the facility and transferred to the storage tank. With the electrolytic cell, chlorine goes directly from the generator into the solution tank.

(3) Economic comparison with the baseline reveals that with on-site chlorine generation, savings over the baseline of $10 million without credits and $12 million with credit are possible. Without on-site generation the corresponding values are $16 and $17 million. Consequently, implementation of aqueous chlorinolysis could save the Army up to $170 million over the baseline for all 10 sites.

3. CONCLUSIONS

The work done on Phase I of this program shows that the chemical approach to the demilitarization of chemical warfare agents is technically feasible and cost effective. In addition, it will provide the government with large amounts of chemicals that might be hard to get otherwise, such as DF. The study conducted here leads one to the following conclusions:

(1) Literature on the chemistry and kinetics of the agents studies is inadequate, especially in the case of mustard.

(2) The information available on the composition of the agents in the munitions is also scarce. The amounts and nature of the solids and other impurities in the munitions must be established because these could have an adverse impact on the chemical methods.

(3) Industry is willing to buy the products from the demilitarization processes at nominal costs. Generally, most companies are not overly concerned about the fact that they are derived from the agents. They are more concerned about purity and the quantities available.

(4) Of all the methods analyzed, anhydrous chlorinolysis and hot water hydrolysis are found to be the best because they are:

- most economical
- can handle all three agents
- produce useful products
- do not create serious disposal problems
- use commercially available and proven process equipment
- can interface with a variety of munition disassembly techniques
- are not labor or energy intensive
- require minimal human interaction
- are highly reliable and use standard chemical and engineering operations.

(5) Anhydrous chlorinolysis and acid hydrolysis are recommended for experimental evaluation in Phase II of this program.

REFERENCES

1. "Operation of the Chemical Agent Munitions Disposal System (CAMDS) at Toole Army Depot" Enclosures 1-21, 1977-1979.

2. Hoffman, F. W. and Reeves, A. M., *J. Org. Chem.* 26, 3040 (1961).

3. Zeffert, B. M., Coulter, P. B., and Tannenbaum, H., *J. Am. Chem. Soc.*, 82, 3843 (1960).

4. Coe, Perry, and Brown, *J. Chem. Soc.*, 3604 (1957).

5. Green, M. and Hudson, R. F., *J. Chem. Soc.*, 1004 (1963).

6. Cadogan, J. I. G., *J. Chem. Soc.*, 3067 (1961).

7. *Organic Chemistry*, Frederick G. Bordwell, McMillan Co. p. 214 (1964).

8. D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

9. DeBruin, K. E. Private Communication.

10. Horner, L., Beck, P., and Hoffman, H., *Ber*, 92, 2088, (1959).

11. Pass, F. and Schindlhauer, H., *Monatsh Chem.*, 90, 1948, (1959).

12. Rumpel, W. *Mitt Chem. Forschungs Inst. Ind. Oster*, 4, 13 (1950).

13. Loewenthal, M., Schweiz, Z. *Pathol u. Bakteriol* 12, 313 (1949) (Chem Abstracts 45, 26031 (1951).

14. "Decontamination Methods for HD, GB, and VX--A Literature Survey" Yurow, H.W., ADB057349, April (1981).

15. "Review of Analytical Procedures for GB, VX, and Their Degradation Products," Crabtree, E.V. and Sarver, E.W., EATR-4490, January 1977.

16. Dr. Joseph Epstein, Private Communication.

17. "Demilitarization of Mustard Agent by Conversion to a Polysulfide Polymer," Davis, T.H., Final Report, Thiokol Corp., Contract No. DAA15-76--0046, 1976.

18. "Demilitarization of Mustard Agents by Conversion to Polysulfide Copolymers with Dichloroethyl" Vrieson et al. Final Report, Thiokol Corp., Contract No. DAAA-0377-M-1586.

18a. "GB-DF Conversion Studies," Vol. 2, Curran et al. Battelle Columbus Laboratory, Contract No. DAAK11-80-C-0068, 1981.

19. Ref. 1, Enclosure 2.

20. Larson L., *ACTA Chem. Scand.* 11,1131 (1957).

21. Dr. Joseph Epstein, Private Communication.

22. Epstein, J., Callahan, J. J., and Bur, Y.E., *Phosphorous*, 4, 157 (1957).

23. "The Rate of Hydrolysis of Mustard Gas and Some Related Compounds." Hine T. B., and Hartnett, J. G., EACO 301, Info. Div. CWS Tech., January 1970.

24. *Modern Cost Engineering Technique* Popper, H., McGraw Hill Book Company (1970).

25. "*Modern* Cost Engineering." Published by *Chemical Engineering Magazine* (1979).

26. *Study of Catalytic and Thermal Decomposition of Toxic Agents* Book 1, Cheselske, F. J., CB-67-2378-10.1.

27. "An Investigation of the Thermal Decomposition of Bis (2, ethylhexyl) hydrogen phosphite and Agent VX as Vapor at Elevated Temperatures" R.R. Lapp and C.J. Schneider. Report No. GM-1592-G-5, Contract No. DA18-108-CML-6628, May 1962.

28. "Thermal Decomposition of 2,2'-Dichlorodiethyl Sulfide" Williams A.H., *Journal of Chemical Society*, 318, 1947.

29. "Reaction of Sarin with Bleach in Dilute Aqueous Solution" Medical Laboratories Research Report No. 379, Contract No. DTIC-AD-047570, July 1955.

30. "Search for Non-corrosive Decontaminants for VX and Application to Demilitarization Operation" Davis G. T. et al ARCSL-TR-78028, July 1978.

APPENDIXES

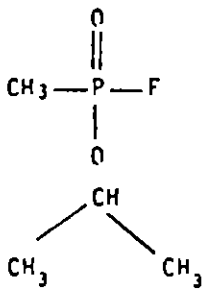
APPENDIX A. LITERATURE REVIEW

Part 1. Chemical Structure and Bonding of CW Agents

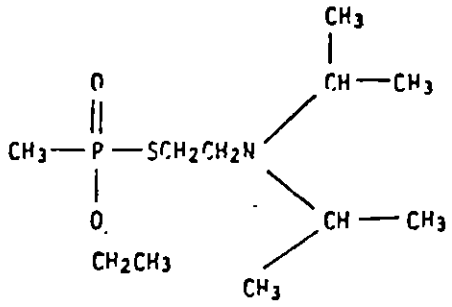
1. INTRODUCTION

The objective of this appendix is to review the chemistry of H, GB and VX as it relates to the objectives of this demilitarization program. The discussion presented here is based on information we obtained from the comprehensive literature search, discussion with consultants, and our views. References cited here are given at the end of this appendix.

The three agents, H, GB and VX, represent three unique structures. GB and VX are structurally related in so far as they both contain tetraco-ordinated phosphorus (pentavalent) and they both have a methyl group attached directly to phosphorus. GB contains fluorine. VX has both sulfur and nitrogen in its structure as shown in Figure A-1. The agent, H is a diethyl sulfide with two chlorine substituents at the terminal carbons.



GB



VX

$ClCH_2CH_2SCH_2CH_2Cl$

H

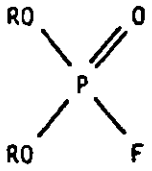
Figure A-1.

At the conceptual level, it appears that the uniqueness of the structural features should represent unique chemistries that one could take advantage of for the purpose of chemical demilitarization. Therefore a brief discussion is presented here on what structural features of these molecules are responsible for their toxicity. This information is relevant in so far as any new chemistry would have to focus on altering those very features that make these molecules toxic, in order that one may eliminate or lessen the toxicity to the levels acceptable for whatever subsequent uses they may be considered.

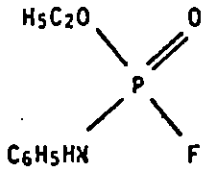
The chemistry of these molecules is discussed in detail in this report to provide a good background on the subject for the development of new concepts and to help identify compounds that could be derived from the agents which may find potential use in other areas within or outside the military.

2. CHEMICAL STRUCTURE AND TOXICITY

During the second world war, B.C. Saunders and his group worked on esters and esters amides of phosphoric acid fluoride.[1-3]



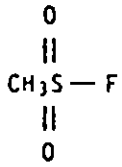
(1)



(2)

R = i Propyl; Sec. Butyl

Their work remained secret until after the war and was known only to the Ministry of Supply. Their work emphasized the pharmacological properties of the alkyl fluorophosphates. Independently of the above group, G. Schrader in Germany had long been working on acid fluorides in search for compounds with acaricidal and aphicidal properties. In this area he was first successful with methane sulfonyl fluoride[4-6] (3) which is still used today in special cases as a fumigant.

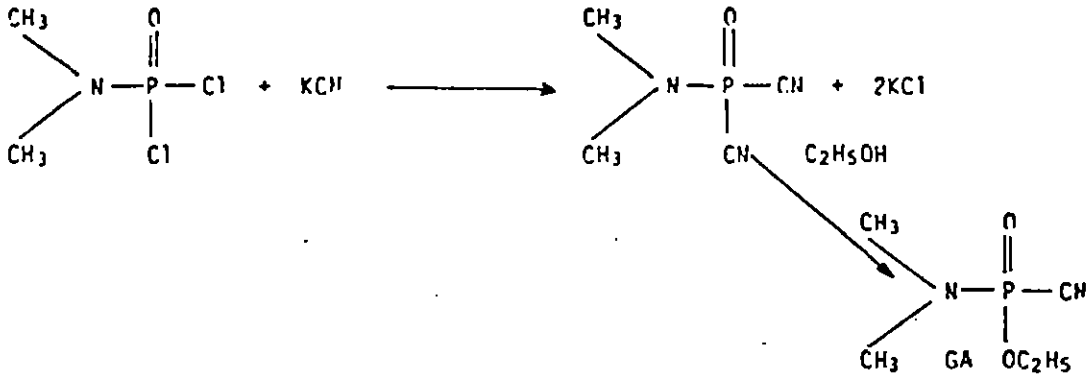


(3)

By changing from sulfuric acid to phosphoric acid he produced a series of compounds with extreme toxicity and this area of research became later his area of interest. As starting material he used N,N dimethylphosphoramido dichloridate (4) which is easily convertible to the difluoride by treating with KF.[7-10]

(4) (5)

Interestingly enough, the difluorides of N,N dimethylphosphoramidates (5) were found to have only weak insecticidal properties.[11] However, when he reacted compound (4) with potassium cyanide the highly toxic and miotic Tabun (GA) was produced[12,13].

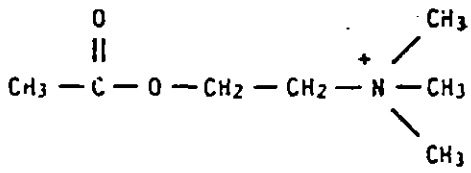


On replacing the dialkyl amino group of GA by an alkyl group (methyl) and the cyano group by fluoride, Schrader synthesized the physiologically extremely potent compound GB.[14] Because of their extreme mammalian toxicity these compounds were not used as insecticides.[15] These phosphonic esters are related to the compounds investigated by Saunders et al.[16]

The anticholinesterase property of organophosphates were first discovered in 1941 by a British group: Adrian, Feldberg and Kilby, who published their findings in 1947.[17] The work originated with the pupil constricting effects of compound (1) (P = i Propyl), which they found were purely local in the case of vapor treatment. They studied various smooth muscle contracting compounds, and found that compound (1) behaved like eserine in that it produced a contraction slowly and progressively and the contraction was not readily

reversed by washing the preparation. Since eserine had long been known as a potent anticholinesterase, they examined compound 1 as an anticholinesterase and found that it was even more potent than eserine.

The role of structure and activity amongst acetylcholinesterase inhibitors is too involved to be dealt with adequately here. The discussion is limited to the structure of GB and VX and their presumed action on acetylcholinesterase. Two regions can be identified on the active site of acetylcholinesterase one of which is called the esteratic site and the other is called the anionic site. The esteratic site, which contains a histidine, serine and a tyrosine in close proximity is responsible for the hydrolysis of the natural substrate, acetylcholine (6). The anionic site, which contains



(6)

an ionized carboxyl group of aspartic acid, is required for proper binding of the molecule at the active site. Figure A-2 illustrates the steps in the hydrolysis of acetylcholine (6) by the enzyme. Figure A-3 shows the steps in the reaction of GB with the enzyme. As can be seen, GB interacts at the esteratic site of the enzyme resulting in phosphorylation of the serine hydroxyl of acetylcholine esterase, apparently by the same mechanism by which acetylation of this serine takes place when the natural substrate is involved. The principal difference is that the reverse reaction--dephosphorylation--proceeds exceptionally slowly compared to deacetylation.[18,19] As a result, the so called "irreversible" inhibition of the enzyme occurs.

Figure A-4 indicates the steps in the reaction of VX with the enzyme. It is clear that unlike GB, the VX molecule is designed to fit the active site of the enzyme more like the natural substrate. VX not only reacts at the esteratic site, but also binds to the anionic site. If one were to introduce a similar side chain on GB, instead of the isopropyl group, then one would expect the molecule to be even more toxic than GB, because it will be taking advantage of not only the esteratic site, but also of the anionic site of the enzyme. Indeed, this molecule, cholinylmethylphosphono fluoridate (7), was

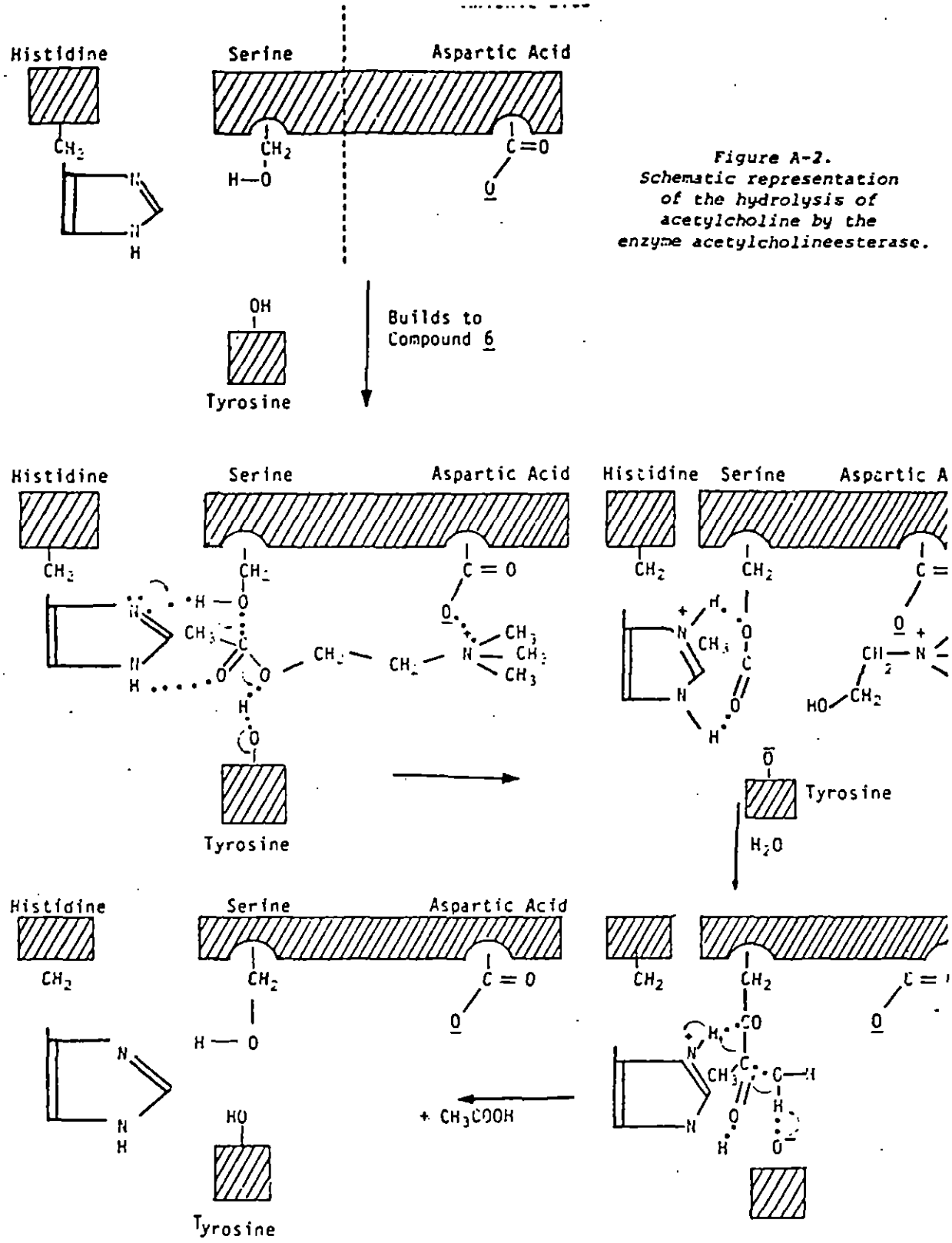


Figure A-2. Schematic representation of the hydrolysis of acetylcholine by the enzyme acetylcholineesterase.

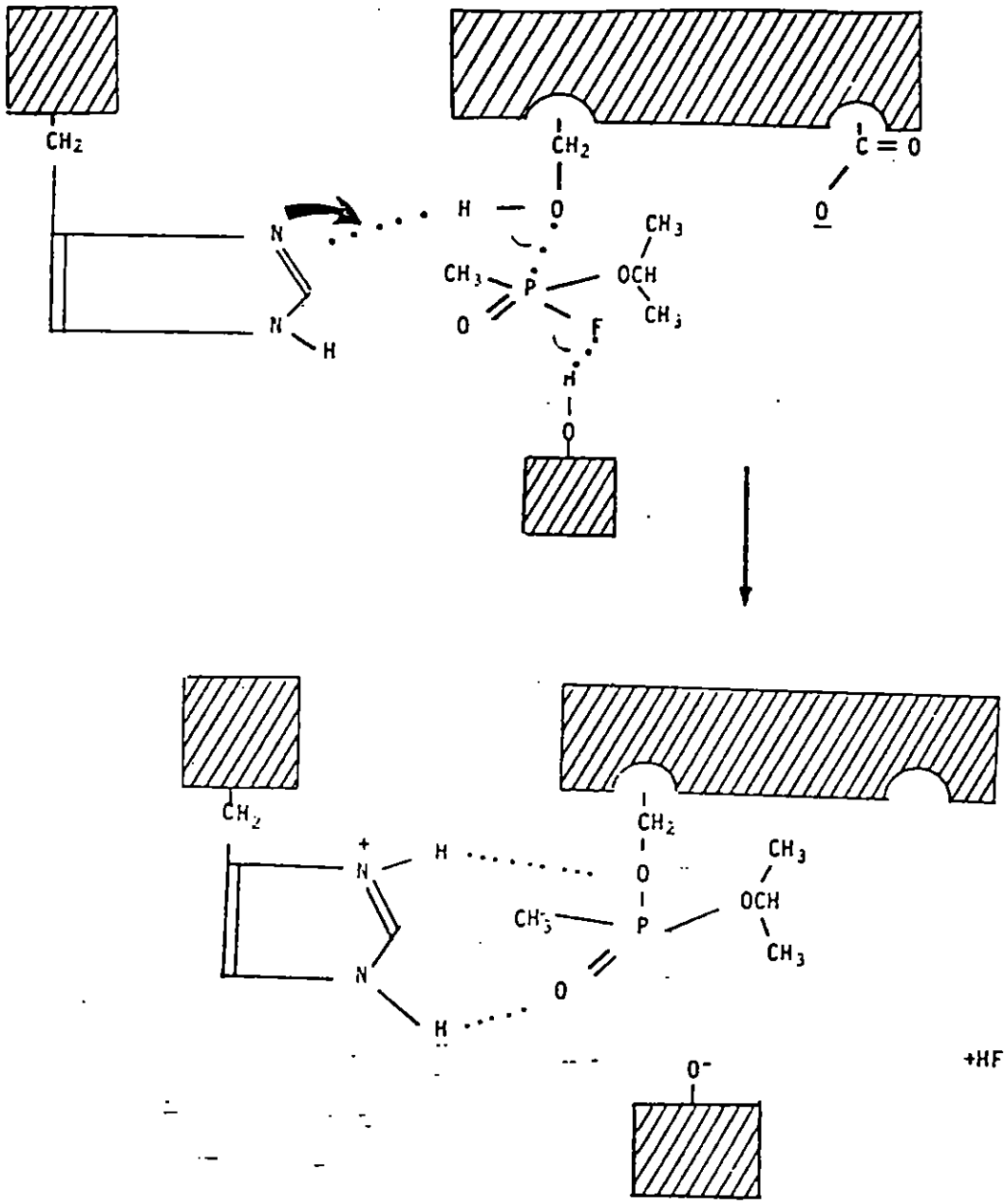


Figure A-3. Schematic representation of the phosphorylation of the serine on the active site of the enzyme acetylcholineesterase by GB.

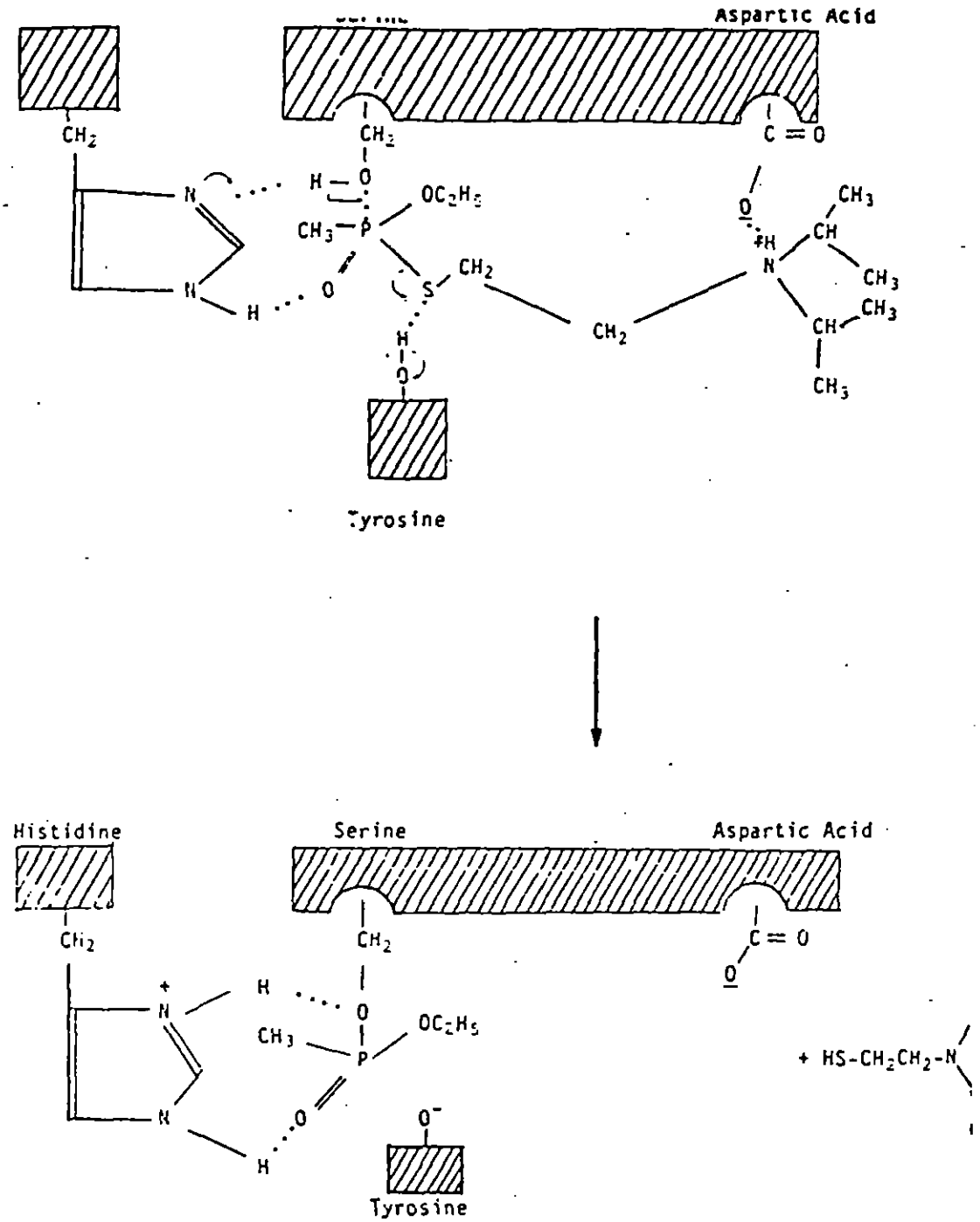
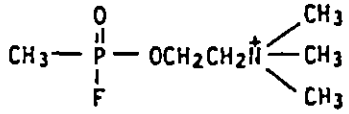


Figure A-4. Binding of VX on the active site of acetylcholineesterase and the subsequent reactions.

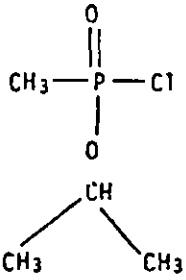
synthesized by Tammelin and Enander[20] and is thought to be the most toxic phosphonofluoridate ever synthesized.



(7)

Toxicity of H has not been identified with any specific enzyme. It is known to be a good alkylating agent. The alkylating property and its vesicant power is lost if the halogen is removed from the molecule.

From the discussion so far it is seen that toxicity of GB and VX can be influenced by many factors. They can be considered as phosphorylation agents which have high specificity for acetylcholine esterase. The word phosphorylation is used to cover displacement at the phosphrous atom of derivatives of phosphinic, phosphonic, and phosphoric acids. The nucleophile present on the enzyme active site would attack the phosphorus with the expulsion of the better leaving group. However, if the leaving group is made extremely reactive, the compound would by hydrolyzed or metabolized before it reaches the enzyme active site. In the case of GB, for instance, removal of fluorine by chlorine, would result in a compound which is considerably less toxic than GB. Similarly, replacement of the P-S bond in VX, by chlorine would result in a less toxic

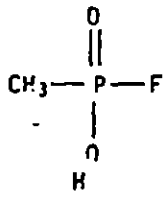


Chlorine analog of GB

compound for several reasons besides the lability of the P-Cl bond, the most important of which being the loss of specificity to the enzyme active site. Indeed the majority of the demilitarization concepts, if not all, rely on

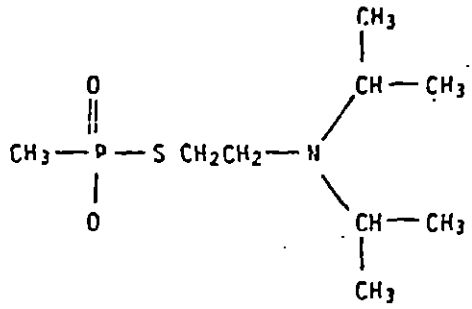
replacing the fluorine in GB and the sulfur in VX by various hydrolytic procedures.

Size, shape, and polarity are very important to the stability of the initial enzyme-substrate complex. Removal of the isopropyl group form GB would result in compound (8) which should be far less toxic than the parent compound (GB), because in the absence of the hydrophobic group, the resulting molecule should



(8)

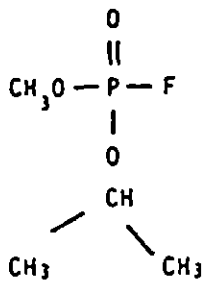
be far less specific to the enzyme or enzymes. In the case of VX, however, the substituent that makes the molecule most suitable for the enzyme active site is the N,N diisopropylethylmercapto grouping. Therefore removal of the ethyl grouping on oxygen in VX would still result in a molecule that exhibits considerable toxicity (9).



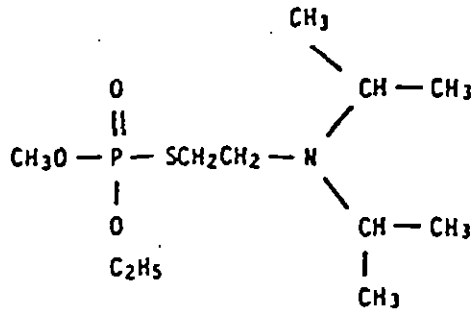
(9)

Replacement of the methyl group attached to phosphorus, in both GB and VX, by an ($-OCH_3$) group while the rest of the molecule remains the same, would decrease the toxicity by an unacceptably small amount (10 and 11). Since the C-P linkage is the most stable of all the bonds in GB and VX, any modifications in this portion of the molecule are very difficult to bring about without affecting the rest of the molecule.

Finally, the modification at the phosphoryl oxygen. As long as the



(10)



(11)

phosphorus atom remains tetracoordinated the possible modifications would involve replacement of oxygen by a less electronegative element like sulfur. In the case of insecticides, the transformation P=S to P=O in tetracoordinated phosphorus almost without fail results in molecules with increased toxicity. Therefore, removal of P=O by P=S should result in molecules with lesser toxicity. However, this lesser toxicity might still be unacceptably high and thus such transformations may not be of value. The complete removal of the phosphoryl oxygen would reduce the molecule to a substituted phosphine, in which phosphorus is tricoordinated. Such a transformation, if it occurs, should completely alter the chemical and biological properties of the molecule.

As mentioned earlier, the toxic action of H is not limited to any single enzyme. H is a universal poison that affects cells of all the tissues with which it comes into contact. Amongst the enzymes, H has the strongest inhibiting action towards the enzyme hexokinase, which regulates carbohydrate metabolism. There is a weak anticholinesterase action. The most pronounced correlation between structure and activity in mustards has to do with the alkylating property of H and its physiological activity. H not only interacts with the protein system of the cell, disturbing its functions down to complete denaturation, but also actively reacts with nucleic acids, in particular with adenine and guanine nucleotides. Thus H, by alkylating nucleic acids, changes their structure and even cross links chains of nucleic acids. The mechanism

of physiological action of H resembles the action of ionizing radiation which changes the functions and structure of the cells.

Among the halogenated sulfides with the structure R-S-CH_2CH_2X, where X is halogen, the highest toxicity is observed when x is chlorine. Bromine derivatives are less toxic and iodine derivatives are even less toxic than the bromine derivatives. Fluorine containing sulfides are non toxic, in sharp contrast to the halogen esters of phosphates where the toxicity is maximum with fluoro compounds and negligible with other halogens.

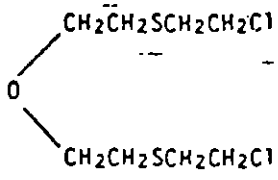
$$RSCH_2CH_2F << RSCH_2CH_2I < RSCH_2CH_2Br < RSCH_2CH_2Cl$$

$$\xrightarrow{\text{Toxicity Increases}}$$

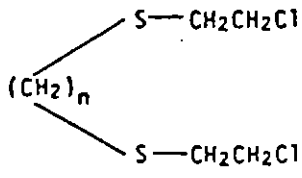
The degree of toxic action also depends on the position of the halogen with respect to the sulfur atom, i.e., on the number of methylene groups between sulfur and halogens.

$$RS(CH_2)_n^X \qquad x = Cl;\ n = 1,2,...$$

The highest toxicity is exhibited when the number of methylene groups between sulfur and halogen is two (n = 2 in the above formula). Compounds where n = 1 and n = 3 are far less toxic than H (n = 2). It has been demonstrated that all organic derivatives of bivalent sulfur which contains a 2-chloroethyl group are toxic. In all these cases, changes in the chloroethyl-structure, such as the replacement of hydrogen by other alkyl groups, by halogen, or other functional grouping, the introduction of a multiple bond and so on leads to a decrease in the physiological activity down to a complete loss of toxic properties. Further, the degree of toxic action depends on the structure of R in addition to the presence of the 2-chloroethyl grouping. For instance, compound (12) is



(12)



(13)

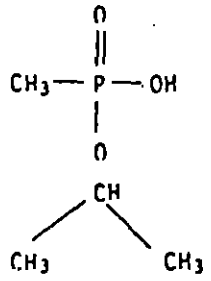
3.5 times more toxic than H whereas in compound (13) the highest toxicity (~5 times more toxic than H) is seen when the number of methylene groups separating the sulfur is two (n =).

To summarize this section, removal of the fluorine from GB by another halogen or oxygen would result in non-toxic products. Removal of the isopropyl group from GB would result in non-toxic, but reactive products. Further, there is no easy way to modify the C-P or the P=O linkages.

In the case of VX, removal of the substituent or sulfur should result in non-toxic compounds. If the ethyl substituent is removed, a toxic compound would be formed. Just as in the case of GB, there is no easy way to modify the C-P or the P=O linkages.

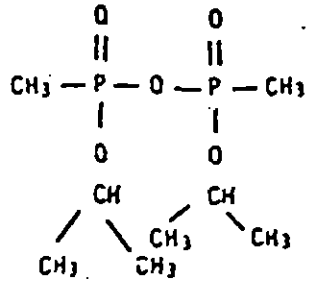
In the case of mustard, the removal of halogen seems to be the way to obtain non-toxic products. Catalytic desulfurization would of course produce non-toxic products. However whether this could be done while the halogen is still present on the molecule remains to be seen.

Before concluding this section a few words on the toxicity of some of the products formed during demilitarization should be addressed. For instance, compound 14 derived from hydrolysis of GB, is non-toxic. However, if processing is done at a high temperature



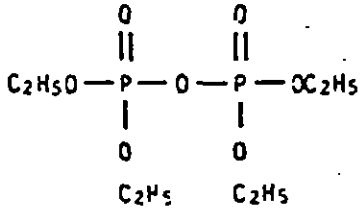
(14)

then (14) could condense by dehydration to give compound 15, which has a structure very similar to compound 16 which had been synthesized



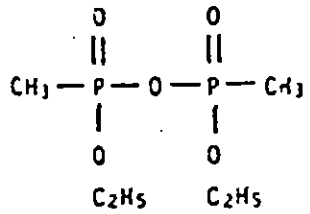
(15)

by Ph.De Clenont in 1354[21] and was shown to be extremely toxic in 1934.[22]



(16)

Similar comments on toxicity is applicable to compound 17 which can be derived from non-toxic products of hydrolysis of VX under dehydrating conditions.



(17)

3. ELECTRONIC STRUCTURE AND BONDING

The chemistry of phosphorus and its compounds follows closely the electronic structure of the atom which is compared with that of nitrogen in Figure A-5.[23] The electronic structure of phosphorus is $1S^2 2S^2 2p^6 3S^2 3p^3$ and that of nitrogen $1S^2 2S^2 2p^3$. As can be seen from Figure A-5 the d-orbitals of nitrogen and phosphorus lie near the continum and other high energy states like 4S, 4p, and 5S are energetically so close together that they may make similar contributions to the 3d-levels in stabilizng these systems. These contributions from higher energy states would affect the polarizability of the atom and hence its reactivity, but the 3d levels of phosphorus is unlikely to influence the stereochemistry of the 5 and 6 coordinated compounds significantly.

The 3s-3d promotional energy for phosphorus is 17 e.v which is significantly less than that of nitrogen (23 e.v). Therefore the contribution of higher energy levels will be greater in phosphorus leading to a reduced electronegativity and greater polarizability. These differences are responsible for the different structures and reactions of the compounds of nitrogen and phosphrous.

For both nitrogen and phosphorus, 3 unpaired electrons are available for bonding and this gives rise to a series of structures closely analogous to nitrogen chemistry. Elemental nitrogen is diatomic whereas diatomic phosphrous molecules are stable only at high temperatures. Table 1[24] compares the analogous compounds of nitrogen and phosphorus and their bond lengths. The diatomic species P_2, PN, and PO indicated in Table 1 are observed spectroscopically at high temperatures whereas N_2 and NO are stable molecules. HCP has been isolated at liquid nitrogen temperatures. However, it polymerizes well below -100°C.[25] HCN on the other hand is a stable molecule. This virtual disappearance of multiple bonded structures analogous to nitrogen carbon and oxygen is common for the second-row elements. Several reasons have been advanced.[26,27] Whatever the reasons it is safe to assume that structures in the literature containing multiple bonds to trivalent phosphorus in fact represent the empirical formulae of polymeric compounds.

TABLE 1. COMPARISON OF BOND LENGTHS OF NITROGEN AND PHOSPHORUS COMPOUNDS

Phosphorus Compounds	Bond Length (A°)[16]	Nitrogen[8] Compounds[9]	Bond Lengtn (A°)
PH_3	1.42	NH_3	1.015
PH_4^+	1.42	NH_4^+	1.031
P_2H_4	--	N_2H_4	1.47 (N-N)
PF_3	1.52	NF_3	1.37
Me_3PO	1.45 (P-O)[19]	Me_3NO	1.35 (N-O)
P_2	1.89	N_2	1.095
PN	1.49	--	--
PO	1.45	NO	1.15
HCP	--	HCN	1.156 (CN)
PO_3^-	--	NO_3^-	1.24

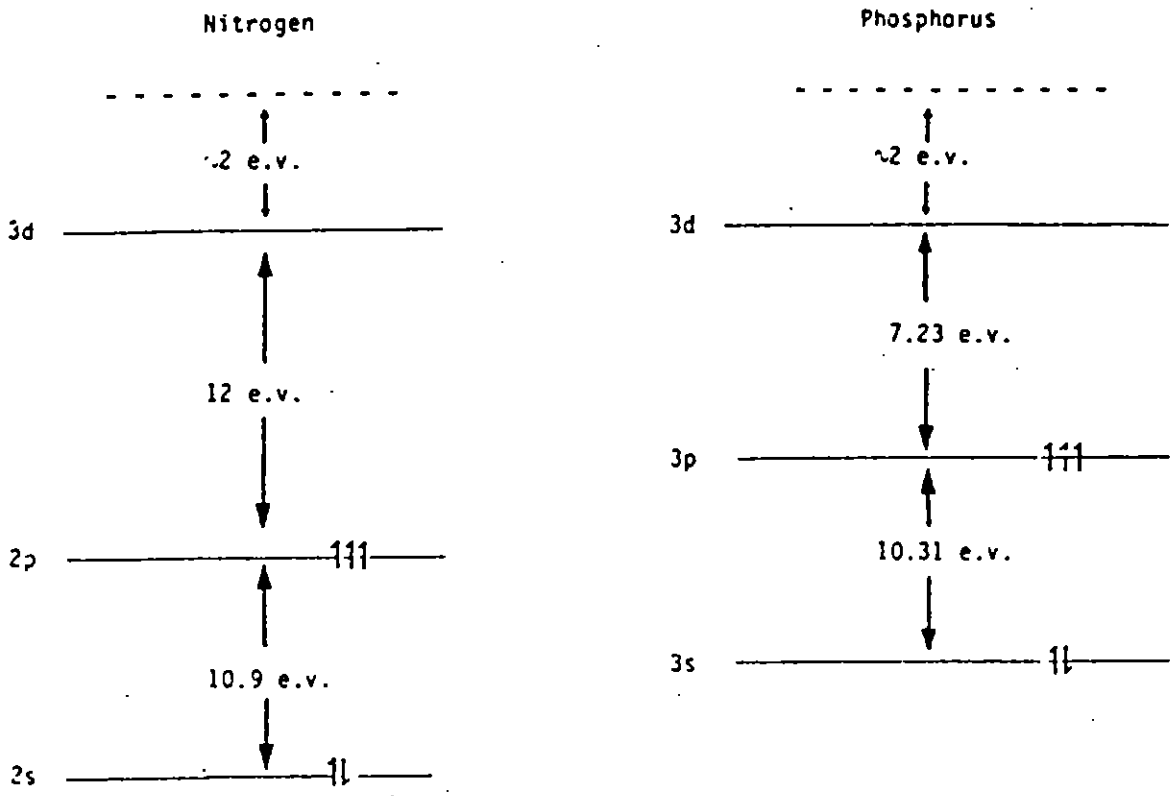


Figure A-5. Atomic energy levels of nitrogen and phosphorus.

Compounds of the type PX_3, expected from the 3 unpaired electrons of 3p level do not form trigonal pyramid molecules corresponding to pure p^3 bonds with bond angles of 90°. Instead, they all form distorted tetrahedrons indicating some participation from the 3s level to form Sp^3 hybridized structures. However, the extent of hybridization is far less in phosphorus compounds compared to nitrogen compounds. The bond angles should be 109°28' for Sp^3 hybridization. For most PX_3 type compounds bond angles are 100 ± 1° whereas for most NX_3 type compounds bond angles are 106-108°. The configuration of tertiary phosphines is more stable to inversion than the tertiary amines and asymmetrically substituted tertiary phosphines can be resolved and are optically stable under mild conditions.

From the above discussion on spatial configurations it is clear that phosphorus is coordinately unsaturated and has the tendency to reach coordination number 5 by forming a new bond with s electrons. This means that in the case of PX_3 compounds such as PCl_3, $RO\text{-}PCl_2$, $(RO)_3P$ or R_3P very reactive nucleophiles are involved which are often used industrially as intermediates for synthesizing derivatives of higher coordination numbers. The resulting products are tetracoordianted phosphorus which possess a tetrahedral structure corresponding to Sp^3 hybridization. Numerically these compounds exceed all other compounds of phosphorus with different coordination numbers by several powers of ten. The electronic structure of sulfur is $1S^22S^22p^63S^23p^4$ which is very close to that of phosphorus except for the fact that phosphorus has three unpaired electrons in its 3p level whereas sulfur has only two unpaired electrons in its 3p level. Just as in the case of phosphorus, sulfur has vacant 3d orbitals available for bond formation. Although the hybridization states of phosphorus are similar to those of sulfur, the tendency of phosphorus to pass into higher binding states is more accentuated than that of sulfur.[28] Atomic energy levels of sulfur are shown in Figure A-6.[29] The 3s-3p levels of sulfur are separated by 12.83 e.v compared to 10.31 e.v for the separation of 3s-3p levels of phosphorus. Both in H and VX sulfur participates in bonding with the valence state of sulfur remaining 2, pricipally with the two unpaired electrons in the 3p orbitals (Sp^3 hybridization contributing considerably too).

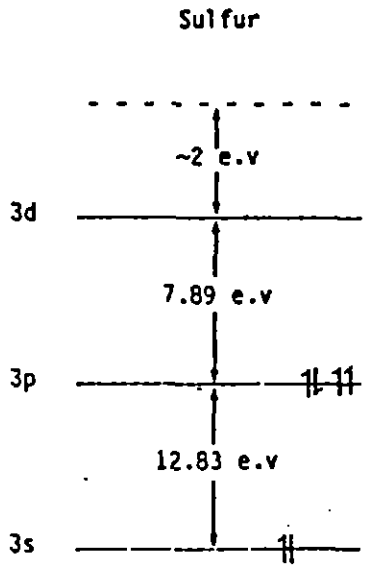
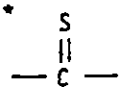


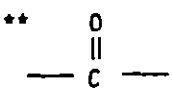
Figure A-6. Atomic energy levels of sulfur.

In an earlier paragraph there was a comparison of the chemistry of phosphorus with that of nitrogen which has a similar electronic arrangement in its outermost shell. A similar comparison can be made in the chemistry of sulfur with that of oxygen which has electronic configuration ($1S^2 2S^2 2p^4$) similar to that of sulfur. Most of the chemistry of sulfur can be rationalized in terms of its having in its lowest valence state, like oxygen, two unshared valence-shell pairs, but compared to oxygen a relatively large atomic core.

The presence of lone pairs on divalent sulfur accounts for the formation from sulfides of sulfonium salts, sulfoxides, and sulfones. It accounts also for the donor properties of sulfur towards Bronsted acids, in the formation of hydrogen bonds; towards Lewis acids, in the formation of face-centered bonds; and towards acidic carbon atoms, in carbonium-ion stabilization, anchimeric effects (which are important in the chemistry of H) and enhancement of electrophilic aromatic substitution.

The large atomic core, compared to oxygen, accounts for the formation of relatively long bonds to sulfur (longer than those to the corresponding oxygen compounds). The large volume of sulfide groups compared to oxygen groups, the large volume of thiocarbonyl groups* compared to carbonyl groups,** the low ionization potential of unshared electrons in sulfur compared to oxygen, and the low electronegativity and electron-withdrawing inductive effect of sulfur compared to oxygen are all examples of that. The sulfur kernels' size is due in part to diminished nuclear-nuclear repulsions, for the formation of sulfur-sulfur bonds at the expense of oxygen-oxygen bonds. Sulfurs' kernel, unlike oxygen, can accommodate in its valence-shell, more than four localized electron-pairs. In other words, sulfur can expand its octet. This ability of sulfur for incipient octet expansion accounts for the formation of such compounds as SO_2, SO_3, SF_4, SF_6 sulfoxides, and sulfones. It also accounts for the activation of protons on adjacent or conjugated centers and in general for the action of sulfur centers as carbanion stabilizers as in the heightened acidity of parasubstituted phenols and toluenes and in enhanced rates of decarbonylation, base catalyzed elimination reactions, and additions to and isomerization of double bonds. Because the sulfur atoms in their lower valence states have both basic sites (unshared valence shell electrons) and acidic sites (coordinately unsaturated atomic cores), they have a high tendency to react with each other to form sulfur-sulfur bonds. Finally, although the electronegativity of sulfur is less than that of oxygen, a lone pair site on sulfur is less basic than oxygen, owing to the sulfur atoms large kernel, which allows unusual angular dispersion of sulfur's unshared electrons. The diffused and polarizable character of sulfurs' unshared electrons accounts, not only for the relatively low basicity of the atoms unshared electrons, but also for the lessened participation of sulfur in resonance stabilization of α-carbonium ions compared to oxygen. It also accounts for sulfur atoms' effectiveness in accommodating negative charge, becoming thereby a relatively good leaving group as manifested for example in the greater stability of thiolate ions compared to alcoholate ions, the readiness of thiocarbonyl compounds to form tetrahedral intermediates and the relatively large barrier to rotation in

* 

** 

carbon-nitrogen bond in sulfur analogues of amides and finally it accounts for the transfer of oxygen atom from sulfides to trivalent phosphorus.

The only other element whose electronic structure and bonding is sufficiently unique to need discussion in this section is that of fluorine. Fluorine is different from other halogens either in the elemental state or bonded in chemical compounds. Fluorine is the most electronegative element. When bonded to other atoms, fluorine polarizes the bond, drawing electrons toward it. This electron-attracting inductive effect of fluorine is clearly seen by the enhanced acidity of acetic acids when substituted by fluorine. All fluorinated acetic acids are stronger than the corresponding chlorinated acetic acids, confirming experimentally the relative electronegativities of fluorine and chlorine. Elemental fluorine is unique in that no other element has greater oxidizing power. The bonds formed by fluorine are amongst the strongest known, particularly to carbon. However, fluorine forms weak bonds to other elements such as nitrogen, oxygen, xenon and so on. In general the strength of the X-F bond decreases as the electronegativity of X increases.[30] Probably the most important characteristics of fluoride ion as compared to other halide ions are charge, size, polarizability, heat of hydration, and thermodynamic properties in solution. Fluoride ion is significantly smaller than other halide ions. Therefore the charge per unit volume is significantly larger for fluoride than for the other halide ions. As a result, the fluoride ion will more strongly affect centers of positive charge. A direct consequence of the small size of the fluoride ion and high resultant charge density is that the fluoride ion, as well as appropriately bonded fluorine atoms, form stronger hydrogen bonds than other ions. The relatively high heat of hydration is also expected from its small size. The inner hydration sphere of the fluoride ion contains five tightly bound water molecules compared with three for chloride and two for bromide.[31] Because the fluoride ion is so tightly bound by water and has such a high heat of hydration, it is extremely poor as a nucleophile in a solvent system containing water. Thermodynamic data on bond energies and heats of solvation can be used to predict that aqueous fluoride ions cannot substitute for chlorides in alkyl chloride.[32] In anhydrous systems, the replacement of chloride by fluoride is strongly favored thermodynamically. The important point of the discussion is that fluoride ion almost always must be anhydrous to achieve fluorination by displacement reactions.

Fluoride ion is a powerful base in many fluoride systems. Many metallic fluorides behave as acids toward fluoride ions and as a result bind them strongly (fluoride ion acceptors).

$$HF + NaF \rightleftharpoons Na^+HF_2^-$$

$$HF + BF_3 \rightleftharpoons H^+BF_4^-$$

$$SbF_5 + SbF_5 \rightleftharpoons SbF_4^+SbF_6^-$$

Finally the exceptionally strong hydrogen bonding ability of fluoride is most clearly seen in hydrofluoric acid. Hydrofluoric acid exists as a polymer $(HF)_n$ which can be either linear or cyclic in the liquid and gas phase.

The high electronegativity of fluorine and the observed electron-withdrawing power in aliphatic compounds would lead to the prediction that fluorine as a substituent on an aromatic ring should be deactivating (i.e., rate retarding) and therefore meta directing towards electrophilic aromatic substitution. However, in fluorobenzene, electrophilic substitution occurs at the ortho and para position and the rate of substitution is only slightly less than the rate for benzene. The classical explanation is that of resonance involving unshared electron pairs on fluorine, just as in the case of oxygen, nitrogen, or chlorine. However this explanation alone is not fully satisfactory. In the resonance representations such as those shown in Figure A-7, fluorine acquires a partial positive charge.

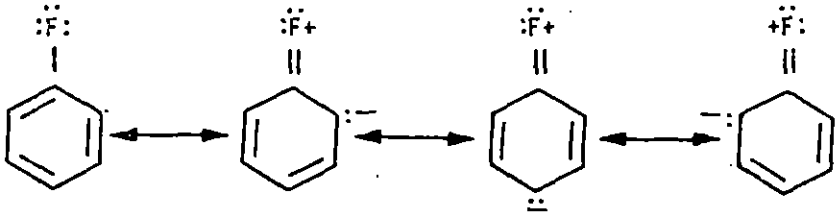


Figure A-7.

Fluorine is so highly electronegative that it is never going to acquire positive charge. Being a first row element it does not have accessible d-orbitals and cannot be easily polarized. The actual situation therefore depends in large measure to the opposing effects of the inductive and resonance influences as shown in Figure A-8.[32] The great electronegativity of fluorine permits it to withdraw electrons from the σ-framework and accumulate electron density on fluorine. This accumulation of positive charge is only partly fed back to the π-system by resonance. The surprising fact is that this resonance feed back in the case of fluorine must be much better than for chlorine or other halogens which do not withdraw electrons as strongly and are much more polarizable and hence would be expected to provide greater resonance feed back. This improved resonance feed back must result from improved orbital overlap. An aryl C-F bond is very short. It is even shorter than a carbon-carbon double bond. This fact in conjuction with the similar size of the carbon and fluorine p-orbitals must account for the better orbital overlap. The above discussion on the resonance possibilities in fluorobenzene serves as a useful introduction on the resonance possibilities in bonds between fluorine and heteroatoms such as phosphorus and sulfur. If the d-orbitals are energetically accessible in the heteroatom, the strong inductive effect of a fluorine or a fluoroalkyl substituent promotes use of some empty d-orbitals to enhance electron withdrawl by resonance.

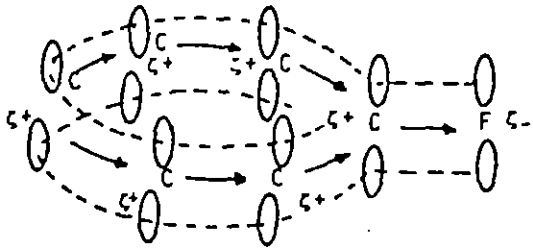


Figure A-8.

4. BOND PROPERTIES AND REACTIVITY

In section 3, the properties of the various elements that constitute H, GB and VX were discussed from the standpoint of their electronic structures. However this approach can only succeed to a limited extent. At present there is no accurate way one could describe the properties of a polyatomic system of the degree of complexity found in GB, VX or HD from electronic structure alone. The purpose of this section therefore is to discuss how the individual bonds in each of these molecules are affected by the rest of the molecule and what is to be expected of their reactivities.

4.1 GB AND VX

The structures of GB and VX are as shown in Figure A-1. The common structural feature between GB and VX is the presence of a pentavalent phosphorus which is bound to a methyl group (the alkoxy group being isopropoxy for GB and ethoxy for VX). The remaining bond differentiates GB from VX. The following discussion concentrates on the circumstances under which each of these bonds can be cleaved and how each bond affects the reactivity of the other bonds in the molecule. Emphasis is placed on a pragmatic comparison of the reactivities and not on the kinetic aspects of these reactions.

4.1.1 P=O; Phosphoryl Oxygen

In both GB and VX phosphorus is in its pentavalent state. They can be represented by the general formula (x,y,z) P=O where x, y, and z are different substituents. In order to satisfy valency considerations, the phosphorus-oxygen bond in the above derivatives were formulated as a P=O, double bond. When G.N. Lewis put forward his octet rule, it was believed that a semi-polar bond P → O should be assumed.[28] However, as early as 1950 there were new thoughts on this problem. Pauling had pointed out that in molybdate ions MoO_4^{--} 3d orbitals of the central atom can form π bonds with 2p orbitals of oxygen.[33] Van Wazer applied these concepts to phosphorus compounds of similar structure.[34] From UV spectra it is possible to show any lack of analogy between P=O and C=O compounds, since n-π* transitions cannot be found in

phosphoryl compounds.[35] Reliable information on the presence of p_π-d_π bonding is not revealed in IR spectroscopy. One of the earliest physical parameters to be obtained for liquid organophosphates is their refractive index. The work of Sayre[36] has shown how one may use bond refraction constants to establish structural identity. Refraction constants have been used by Gillis to show that in phosphates, the phosphoryl oxygen is bound by coordinate rather than double bonds to phosphorus i.e., P → O rather than P=O.[37] A simple electronic picture is given by Lucken and Whitehead[38] for the bonding of the four groups attached to phosphorus in phosphoryl derivative with three substituents. Accordingly the 3s and 3p orbitals of the central phosphorus atom hybridize to four Sp^3 orbitals which form four σ bonds with suitable overlap with the p-orbitals of the substituents. A π-bonding system is superimposed on this σ-bonding skeleton to which phosphorus contributes an electron forming a d_π-p_π bond to oxygen. An oxygen atom bound only to phosphorus, such as the phosphoryl oxygen, participates with three π-electrons whereas an oxygen atom which forms two σ-bonds such as the oxygen of the isopropoxy (GB) or alkoxy (VX) linkage take part in the bonding system with two π electrons. In a series of tetrahedrally constructed compounds, including phosphorus, Cruickshank[39] considered the geometrical properties of two of the five 3d orbitals of phosphorus for the qualitative assessment of bond distances and structural proportions. Collin took into account not only the two strongly bonding orbitals but all five 3d orbitals of phosphorus.[40] The orbital overlap in the phosphoryl P-O bond is illustrated in Figure A-9[41] and the calculations of Craig, et al. assign to the overlap integral sufficiently large value for efficient bond formation.[42,43] If the above results are regarded in the context of how a single oxygen or sulfur atom is bound to the phosphorus, then they also support the formulation of O or S=P, double bond to phosphorus and not that of a semipolar bond. The actual state it would appear is better given by the formulation 18 than by the structure 19.[44] Indeed if one looks at Figure A-9 and takes into consideration

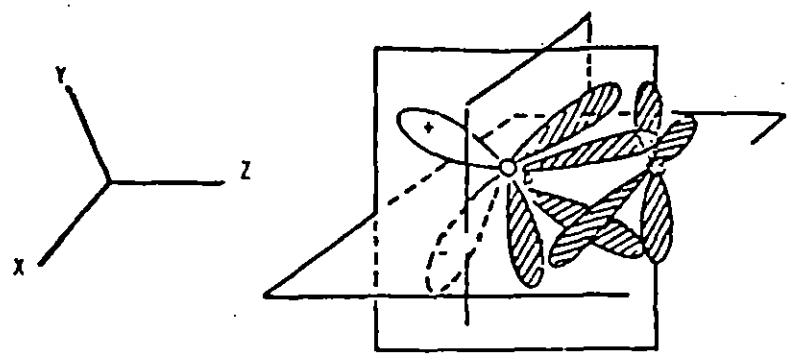
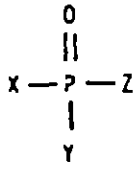
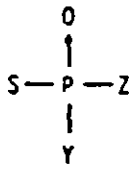


Figure A-9.

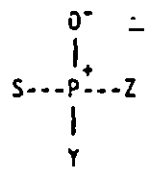


(18)

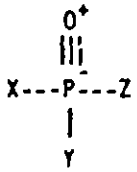


(19)

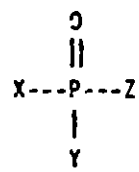
extensive overlap indicated by the calculations of Craig et al. then the P-O bond has the characteristics of a triple bond, rather than those of a double bond, since both pairs of orbitals are equally capable of overlap. Charge transfer to the phosphorus atom is probably far from complete and the oxygen atom retains a net negative charge. In resonance language, the P-O bond is best represented as a hybrid of the canonical forms 20, 21, and 18 with the form 18 having lesser contribution than forms 20 and 21. As far as the reactivity



(20)



(21)



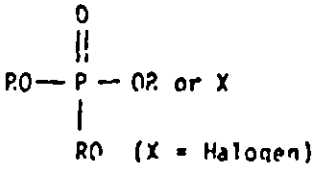
(18)

of phosphoryl compounds are considered, the results of Collier[40] indicate that minor changes in energy (~10 K.cals/mol) is enough to bring about changes in conformation which in turn induce changes in the 2p-3d interaction and thereby the charge distribution. Changes in charge distribution would mean considerable variance in chemical reactivity. If one considers sulfur to be present in the portion of phosphoryl oxygen, then one obtains the thiono-compounds, P=S. Since double bonded sulfur is less electronegative and more readily polarized than double bonded oxygen, the effective charge on the phosphorus is reduced. Therefore the rate of alkaline hydrolysis of thiono derivatives must be lower than that of P=O derivatives, which is a well-known fact in preparative chemistry. It is this decrease in reactivity that makes many an insecticide less toxic as one goes from P=O to P=S or more toxic in the reverse direction i.e., from P=S to P=O, all other factors remaining the same. Although P=O bond has been much more studied than P=S bond, it is generally assumed that the two bonds are of the same type ($\sigma + \pi$) i.e., their formation principle is the same. But the π bond component is much smaller for the P=S bond.[45] P=S bond is polar, possessing a nucleophilic center at the sulfur and an electrophilic center at the phosphorus.

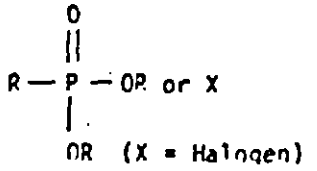
4.1.2 Phosphorus-Carbon Bond

The phosphorus-carbon bond is hydrolytically the most stable bond in GB and VX. This carbon happens to be a methyl group. In this group the carbon happens to be Sp^3 hybridized. There is no possibility for this carbon to participate in π-bonding with phosphorus. The effect of replacing an alkoxy substituent, for instance, by a methyl group is to increase the positive charge on phosphorus. Because, in the alkoxy group, the lone pairs on oxygen can π bond with the d-orbitals of phosphorus and since this effect is stronger than the inductive electron withdrawl by oxygen, the net effect is to decrease the positive charge on phosphorus and make it less electrophilic. In compounds 22, 23, and 24 the alkaline hydrolysis would be progressively faster as one goes from 22 to 24 and acid hydrolysis would be rendered more and more difficult. This has been found to be true experimentally. It is this increased hydrolytic lability that is responsible for the increased toxicity, in general, other factors remaining the same, for phosphonate esters compared to phosphate esters. However, this statement has to be qualified, since

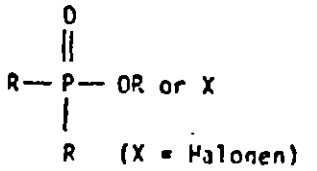
toxicity depends on so many factors that the above factor is only one of the many responsible for increase in toxicity.



22 (Phosphate)

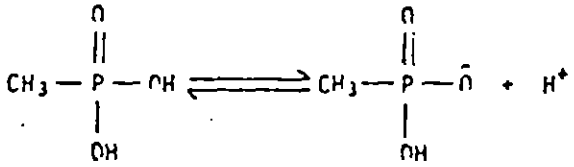


23 (Phosphonate)

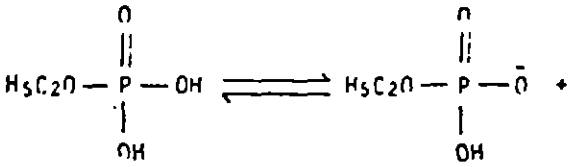


24 (Phosphinate)

The inductive effects of substituent on phosphorus cause variations in dissociation constants of oxyacids of phosphorus similar to those seen with carboxylic acids. Since carbon is less electronegative than oxygen, the replacement of oxygen by carbon would result in a decrease in inductive electron withdrawal. This decrease in inductive effect would be expected to result in a decrease in acid strength. This is found to be true and the first dissociation constants of methyl phosphonic acid (25) and ethylphosphoric acid (26) expressed as pKa's are, 2.3 and 1.8 respectively.[46] The acid



pK = 2.3 (25)



pK = 1.8 (26)

strength decreases generally with substituents in the order H>RO>HO>Ar>R.[47] The special circumstances under which a phosphorus-carbon bond can be cleaved, such as the presence of a halogen β to the carbon attached to phosphorus,[48] or when a highly stabilized carbanion such as p-nitrobenzyl carbanion can be formed as a result of hydrolytic cleavage[49] would not be discussed here as they are not relevant to the GB and VX problem.

4.1.3 Phosphorus-Fluorine Bond

The P-F bond is present in GB, though not in VX. The fact that a fluorine atom is a common feature of many neurotoxic phosphoric acid esters, led to the correlation of this property with the fluoride ion liberated by hydrolysis and inhibition. It was discussed in section 2 that GB contains no group in the molecule which would be suitable for interaction with the anionic site of acetylcholinesterase. Phosphonofluoridates are first and foremost normal acid halides. The fact that phosphorochloridates are not neurotoxic as compared to phosphorofluoridates must therefore depend on the special properties conferred by fluorine. Some of these properties of fluorine were discussed in section 3.

First of all, a phosphorus fluorine bond is a lot more stable than a phosphorus-chlorine bond. The reason for this will be discussed in this section. The d-orbitals in the neutral atom are too diffuse to form useful bonds.[39] Gillespie suggested that modifications occur in molecule formation by polarization due to attached ligands.[50] At first D.P. Craig and co-workers assumed that the d-orbitals on the central atom contract as a result of perturbations due to the attached groups.[42] It was shown that the overlapping power of d-orbitals could account for bond formation only if the orbitals were contracted, and this might happen if the ligand atoms were highly electronegative. Calculations[51] show that fluorine, chlorine and carbon atoms are all capable of contracting the d-orbitals to such a degree that the contracted orbitals could contribute to covalent bonds, in so far as their radial maxima fall at distances comparable to a bond length. The degree of orbital contraction varies with the nature of the ligand in the order F>Cl>C>>H. The first three atoms are more nearly equal in their perturbing power than expected from their Pauling electronegativity. H is ineffective. Concerning the Pauling electronegativity of atoms to their bond contracting power, it was concluded that the Pauling electronegativity was not closely connected to the d-orbital contracting power, although it may well be involved in the stability of the finally formed bond.[51] Fluorine bonds are the most stable. Although chlorine orbitals overlap with the degenerate pair of d-orbitals of phosphorus, the overlap will be less than that of fluorine because of the P-Cl bonds are longer. The higher electronegativity of fluorine combined with its smaller size makes the overlap with d-orbitals more effective.

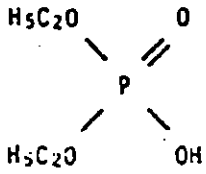
As mentioned in Section 2, the higher stability of P-F bond when compared to P-Cl bonds would ensure that higher concentrations of phosphorofluoridates reach the site of biological action before being hydrolyzed. In addition, the fluorides are more lipophilic than chlorides or bromides. For these reasons they possess superior penetration and partition properties.

So far the discussion has been on the higher stability of the P-F bond compared to the P-Cl bonds. However, in GB, the P-F bond is the most labile bond, hydrolytically. Since loss of fluorine results in loss of toxicity, all demilitarization techniques have emphasized ways to cleave this bond.

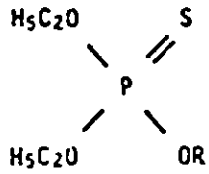
4.1.4 Phosphorus-Sulfur Bond

In VX, the P-S bond that occurs is of the thiolo-form i.e., P-S-C in which sulfur is present in divalent form, as in sulfides. The lowered electronegativity of sulfur, in combination with its diminished ability to π-bond with phosphorus decreases the positive character of phosphorus less than the ester oxygen linkage, P-O-C. In other words a tetracoordinated phosphorus with a thiol ester linkage, as in VX should be more susceptible to nucleophilic attack than one that contains only ester oxygen linkages. This in combination with the fact that a mercaptide ion is a better leaving group than an alkoxide ion makes the P-S bond the most readily cleavable during alkaline hydrolysis of VX. However, the rate of this P-S cleave is much smaller compared to the P-F cleavage in GB. Just as removal of the fluorine from GB results in detoxified molecule, so also the removal of the substituted sulfur portion of VX would result in detoxified molecule. Therefore all the chemical methods of demilitarization have focused on cleavage of this P-S bond by various methods.

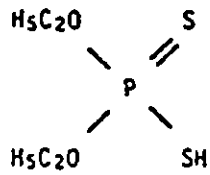
In section 4.1.2 the effect of substituting carbon for oxygen on phosphorus was discussed from the point of view such a change would have on acidity. It was seen that the acidity falls in the order phosphoric > phosphonic > phosphinic. Increasing the sulfur content decreases the acidity in water but increases acidity in alcoholic solution.



(27)



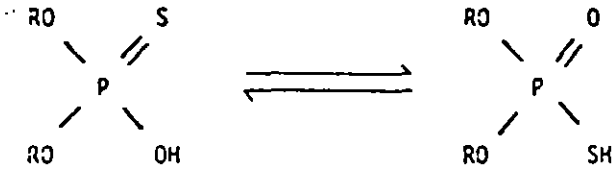
(28)



(29)

7% alcohol pKa =	1.37	1.49	1.55
80% alcohol pKa =	3.15	2.84	2.64

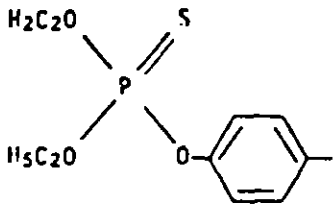
It is now recognized that in sulfur containing phosphorus compounds the following equilibrium, called the thiono-thiol equilibrium, exists



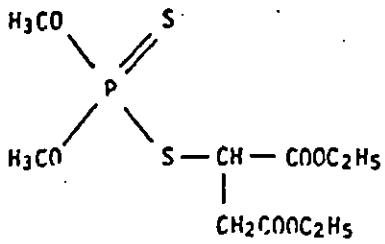
Thiono Thiol

The thiono form becomes increasingly stable in the order phosphoric-phosphonic-phosphinic acid. In 7 percent alcohol solution 80 percent of phosphoric derivative is in the thiol form. However, only 5-20 percent is in the thiol form in 7 percent alcoholic solution of the phosphonate derivative. In phosphinate, under the above conditions thiol form decreases to 0-1 percent. When 80 percent alcohol is used the thiono form is stabilized. At least 93 percent of the thiophosphonic acid is present in the thiono form.

The thiono-thiol isomerization is particularly liable to occur on heating and therefore commonly arises during distillation of such compounds. In compounds like (30) and (31) relatively vigorous conditions are required to produce the isomerization.

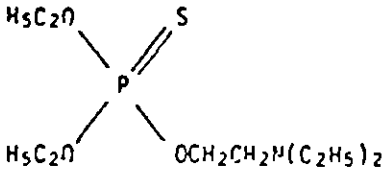


(30)
Parathion

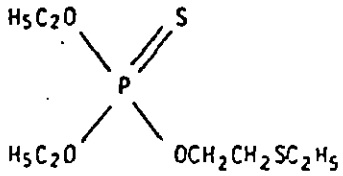


(31)
Malathion

However, the isomerization is rapid in compounds like Tetram (32)[53] and Systox (33).[54]

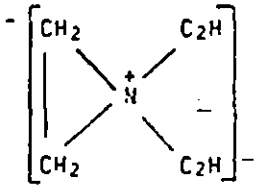


(32)
Tetram

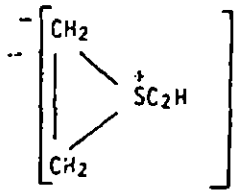


(33)
Systox

It has been postulated that the reason compounds 32 and 33 isomerize so rapidly is because they readily form ionic intermediates such as 34 and 35. The fact that polar solvents, such as ethanol, greatly enhance the isomerization



(34)



(35)

has been used in favor of ionic intermediates.

It was seen in [illegible] 3 that sulfur is extremely susceptible to oxidation. In phosphorus-sulfur bonds the thiono form P=S is rapidly oxidized [illegible]. The thiolo form -S- is the least susceptible to oxidation. However, [illegible] chlorinolysis results in rapid chlorination of this sulfur, followed by hydrolysis to a sulfoxide or sulfone. Chlorinolysis cannot be stopped at this point and the P-S bond is cleaved. This is a rapid and vigorous reaction. The P-S cleavage with nucleophilic reagents is slow when compared with the P-F cleavage. Hence chlorinolysis has been suggested as a means of demilitarizing VX.

4.2 H

The structure of H is as shown in Figure A-1. It is a β,β-bischloroethyl-sulfide. Some of its chemistry has already been anticipated in the discussion in Section 3 on the electronic structure of sulfur and also on the discussion in Section 2 on structure and toxicity. The most significant feature of H is the presence of the sulfide group and that of a chlorine at a suitable distance from sulfur.

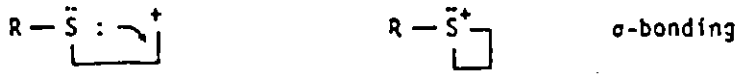
In considering the effect of the sulfide group one may take into account the facts that (1) the electronenativity of sulfur atom is much less than that of oxygen; (2) the unshared electron pairs of sulfur are in 3s-3p or in their hybrid orbitals and hence less tightly bound as compared to the electron pairs of oxygen; and (3) d-orbitals are available for sulfur. The longer bond length and smaller bond angles of sulfur bonds than the corresponding oxygen bond may also be important factors.

The reactions involving carbonium ion may be facilitated by the presence of sulfide group due to ion-stabilization. Two types of stabilization may be considered (1) a π-bonding between sulfur and the α-carbonium ion, and (3) a σ-bonding between sulfur and a carbonium ion generated at a position other than the α-carbon.

The π-bonding can be formulated as in the following "electron-releasing conjugation" involving unshared electrons, and this type of stabilization should be more effective for oxygen than for sulfur, because of the more diffused nature of the sulfur orbital than the oxygen orbital.

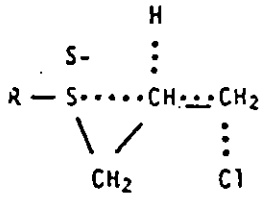
Electron-releasing conjugation

Stabilization through σ-bonding reflects the nucleophilicity of the hetroatom and sulfur is known to be a much stronger nucleophile than oxygen. A stable σ-bonding may result in the formation of sulfonium compounds and a reactive σ-bonding may result in the neighboring group participation of sulfide group.

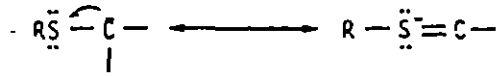


σ-bonding

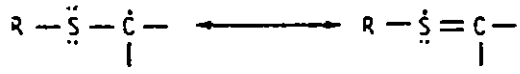
Reactions involving α-carbanion may be facilitated by the presence of electron-withdrawing substituents. A strong electronegative group may stabilize the carbanion by an inductive effect. Electron-accepting conjugation involving



d-orbitals may also stabilize the carbanion, while electron-releasing inductive effect and any repulsion between electron pairs and carbanion may destabilize the carbanion. Whatever the reason, in carbanion



forming reactions sulfides are more reactive than the corresponding esters. For a homolytic reaction, these effects may work in the positive or negative direction, depending on the polarity of the transition state of the reaction.



As mentioned in the case of carbanion forming reactions, sulfides are more reactive than ethers in homolytic reactions.

5. CONCLUSION

This concludes the first part of the literature review. The purpose of this section was to explore at length what type of chemistry is possible given the structures of H, GB and VX. The discussion was carried from first principles to indicate the full range of possibilities within which novel concepts could be formulated. It is apparent from the discussion that in the case of phosphorus containing compounds, GB and VX, highly polar bonds are involved and most of their reactions are going to be heterolytic in nature. Important radical reactions include autoxidation and the reaction of phosphines with olefins. However, these reactions, it would appear, are beyond the scope of the structures defined by GB and VX. The most important reactions of phosphate esters and related compounds are seen to involve nucleophilic displacement at the phosphoryl group or saturated carbon atom. The expected reactions of H are that of a fairly representative member of the class of organic sulfides. The second part of the literature review will discuss the various reactions indicated by the above discussion in detail. The second part of the review will also discuss some of the target compounds that can be derived from GB, VX and H.

LITERATURE REVIEW

Part 2. Chemical Demilitarization of H, GB, and VX

1. INTRODUCTION

In the first part of this literature review[55] the chemistry of the compounds H, GB, and VX were treated from the point of view of their electronic structure and bonding. This was done to define the kind of chemistry that is possible with these compounds in relation to specific bonds in these structures. The toxicity of the various products when specific bonds are modified was also discussed in Part 1.

In order to interpret the reactions of organophosphorus compounds, therefore, a detailed knowledge of the relationship between reactivity and the structure of the nucleophile and the phosphorus compound is required. From a consideration of the nature of bonding in GB and VX, as given in Part, 1 it was seen that the reactions are going to be heterolytic in nature. It was also stated that the most important reactions would involve nucleophilic displacement at the phosphoryl group or saturated carbon atom.

The presence of the P=O phosphoryl bond in GB and VX determines to a large extent the chemistry of these compounds. The formation of the phosphoryl bond creates a large positive charge on the phosphorus atom which consequently becomes highly electrophilic towards the more basic nucleophiles. Indeed, the more important reactions concerned with chemical demilitarization involve one nucleophile or another. The displacement reactions of phosphoryl compounds are similar to the reactions of organic acylating agents.

In addition, the P=O bond, whether regarded as a d_π-p_π or coordinate bond (see Part 1), is highly polar and can consequently participate in nucleophilic displacement reactions as a nucleophile. The relative reactivities of the P=X (where X = C, N, S, or O) bond as a nucleophile is in the order given below.

$$R_3P = CH_2 > R_3P = NR > R_3P = S > R_3P{=}O$$

Phosphine oxides and oxygen esters react as nucleophiles only with very reactive electrophiles, in particular chlorinating agents, e.g., $COCl_2$, PCl_5, and $SOCl_2$. For demilitarization purposes both types of reactions, that is

reactions in which the nucleophile attacks the P atom of the phosphoryl bond and also the reactions in which the phosphoryl group itself acts as a nucleophile, are considered. In Figures A2-1, A2-2, and A2-3 the more important reactions of H, GB and VX, which are of relevance to demilitarization, are shown in a schematic mode. These reactions are discussed in detail in the following sections. Since many of the reactions of GB and VX involve nucleophilic displacement at phosphorus atom, there is a section describing the mechanism of this group of reactions at the very outset. Following this discussion, the different reactions are discussed under the headings of different classes of reactions, like alkaline hydrolysis, acid hydrolysis and so on, in order that it might help to identify a process by following such a discussion.

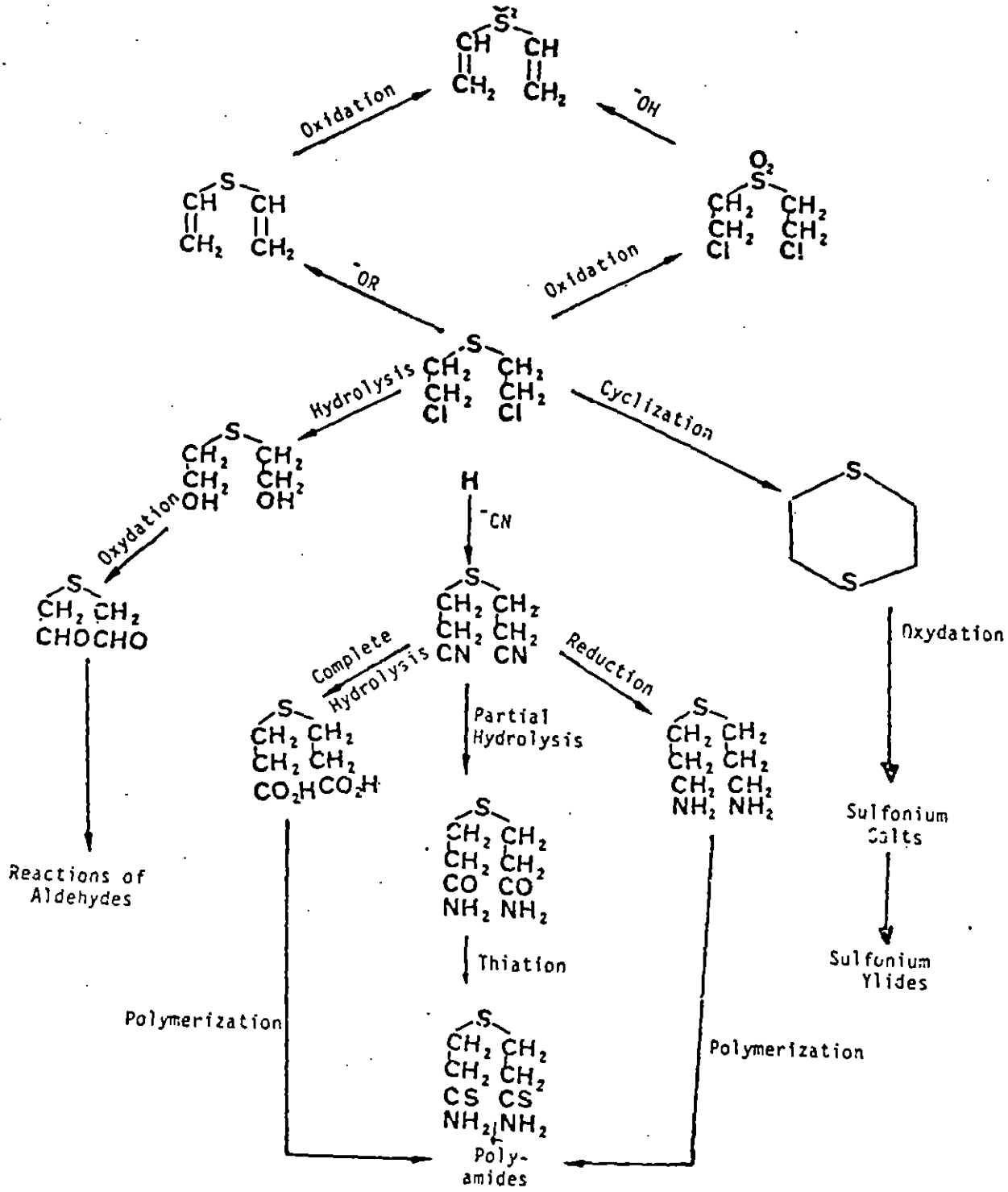


Figure A2-1. Reactions of mustard.

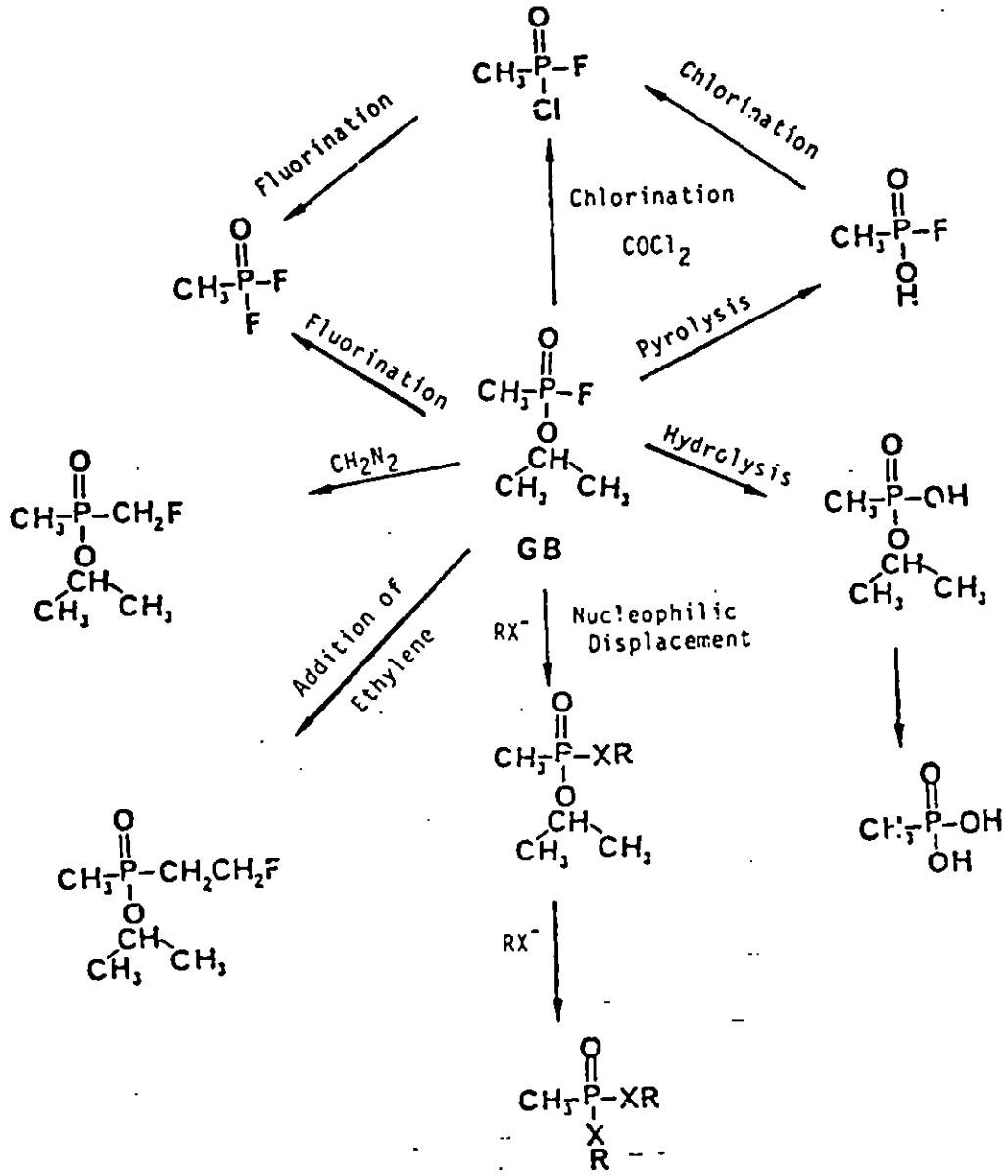


Figure A2-2. Reactions of GB.

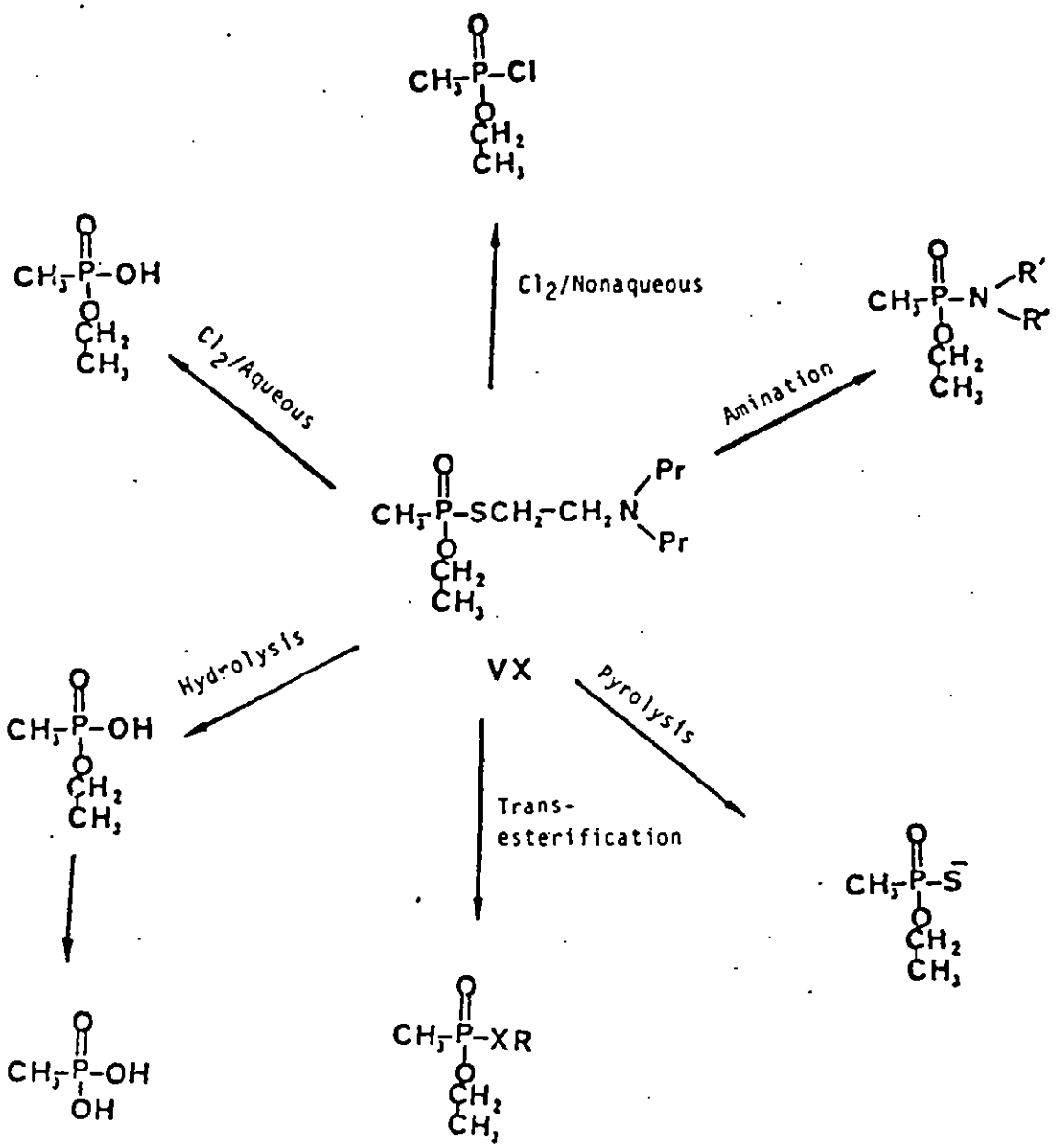
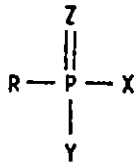


Figure A2-3. Reactions of VX.

2. NUCLEOPHILIC DISPLACEMENT AT PHOSPHORUS

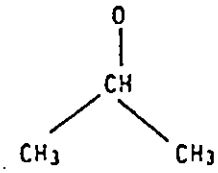
Nucleophilic attack at the phosphorus atom in compounds of the general structure 1 occurs when the atom Z is C, N, O, S, or Se. Examples of attack



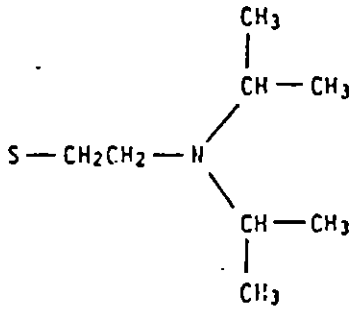
1

on phosphoryl compounds are found in the pioneering work of Hoffmann[56] and Michaelis,[57]

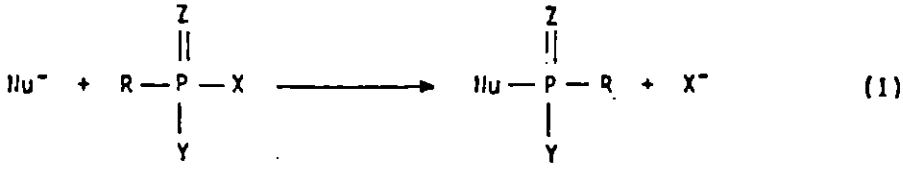
Both GB and VX belong to compounds represented by the general structure 1. In the case of GB, R is CH_3 group, Z is oxygen, X is fluorine, and Y is the isopropoxy group



In the case of VX, R is CH_3 group, Z is oxygen, X is N,N diisopropyl-mercaptoethyl group



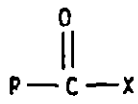
and Y is the ethoxy group CH_3CH_2-O. Nucleophilic displacement at phosphorus in compounds of the generalized structure 1 is given by Equation 1.



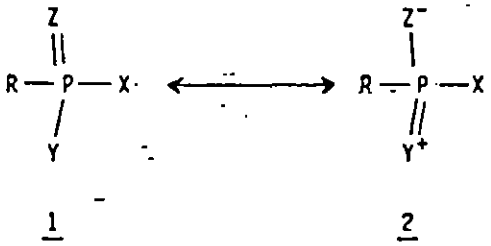
(1)

When the nucleophile Nu^- is $\bar{O}H$, the reaction becomes alkaline hydrolysis. If the nucleophile is H_2O, the reaction becomes hydrolysis by water at neutral pH. If the nucleophile is an amine, the reaction becomes amination, and if the nucleophile is an alkoxy anion, $\bar{O}R$, the reaction becomes transeterification and so on. As far as demilitarization is concerned, reactions of the above type have been the most thoroughly studied.

By analogy with nucleophilic substitution at carbonyl compounds,

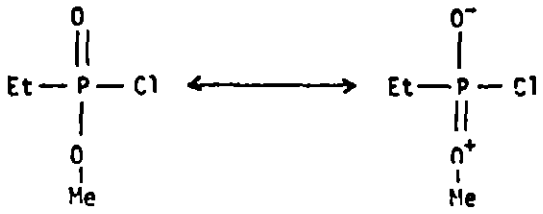


where X is a good leaving group, three possible mechanisms for nucleophilic substitutions at phosphor. can be identified. These are the (1) elimination-addition mechanisms, $S_N1(P)$, (2) addition-elimination, and (3) the $S_N2(P)$ mechanism. Before the analogy with carbonyl compounds are taken too far, it should be pointed out that in structures such as those given by (1) extensive conjugation of the type 1 - 2 does not occur.



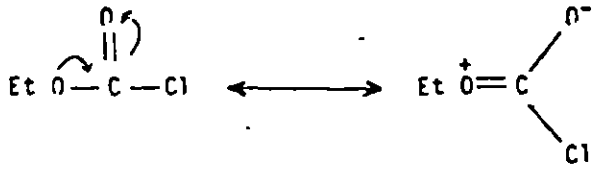
1 2

If R = Et, Z = O, X = Cl and Y = OMe the resonance structures could be written as



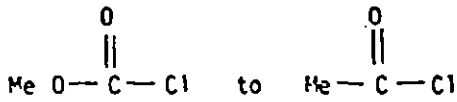
3 4

This is in contrast to the planar carbonyl compounds where the lone-pairs adjacent to the carbonyl group are extensively delocalized as in 5 and 6



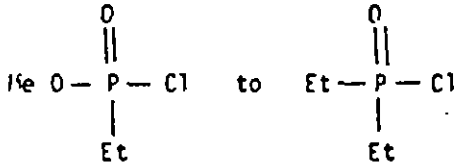
5 6

The result is that minor structural differences have very large effects on the rates of hydrolysis of acyl compounds, but only small influence on the analogous phosphoryl compounds. For instance, going from compound,



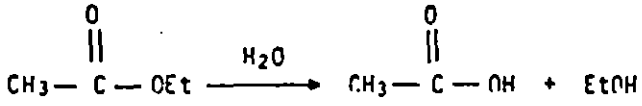
7 8

the rates of hydrolysis are increased[38] by a factor of 10^4 whereas in the case of phosphorus compounds going from

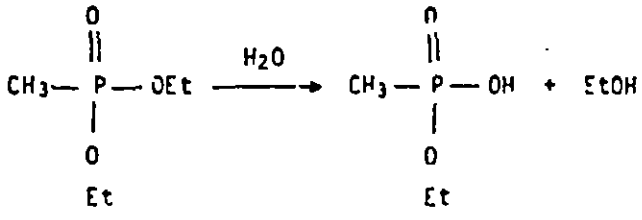


3 9

the rates of hydrolysis are increased only by a factor of 15. Nucleophilic attack at phosphoryl center shows a much greater dependence on the strength of the covalent bond between the leaving group and phosphorus than does attack at a carbonyl center. In the latter case, covalent bond formation with the incoming nucleophile controls reactivity. For instance, when ethylesters of phosphoric and carbonylic acids are hydrolyzed by water, the activation energy of the two processes is much the same.



E_A = 14.1 kcal/mole; $\Delta S^{\neq}$ = -21.1 e.u.

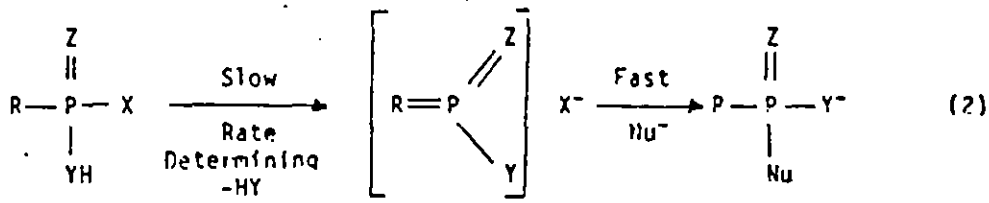


E_A = 13.4 kcal/mole; $\Delta S^{\neq}$ = -33.7 e.u.

The entropy change, on the other hand, is much more negative with phosphoric esters[58] since the steric requirements for approach to a tetrahedral molecule are more exacting than those of approach to a planar molecule and three partially charged oxygen atoms require solvation in the transition state (p_π-d_π bonding to phosphoryl oxygen is interrupted in pentacovalent structures).

2.1 $S_N1(P)$ MECHANISM - ELIMINATION - ADDITION

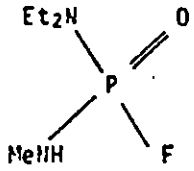
The $S_N1(P)$ mechanism is generalized by Equation 2, and is directly analogous to S_N1 mechanism of carbon chemistry.



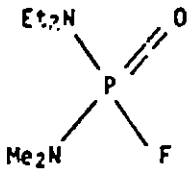
(2)

10

Reactive species like 10 have never been isolated, but their existence as transient intermediates has been deduced from kinetic and stereochemical evidence and one of the best established examples involves the hydrolysis of monoesters of phosphoric acid. In the case of GB and VX the above mechanism can be completely ruled out, since the presence of the C-P linkage precludes the formation of a reactive transient intermediate, such as 10. However, such a mechanism is invoked to account for the fact that Compound 11 is hydrolyzed almost 10^4 times faster than Compound 12.

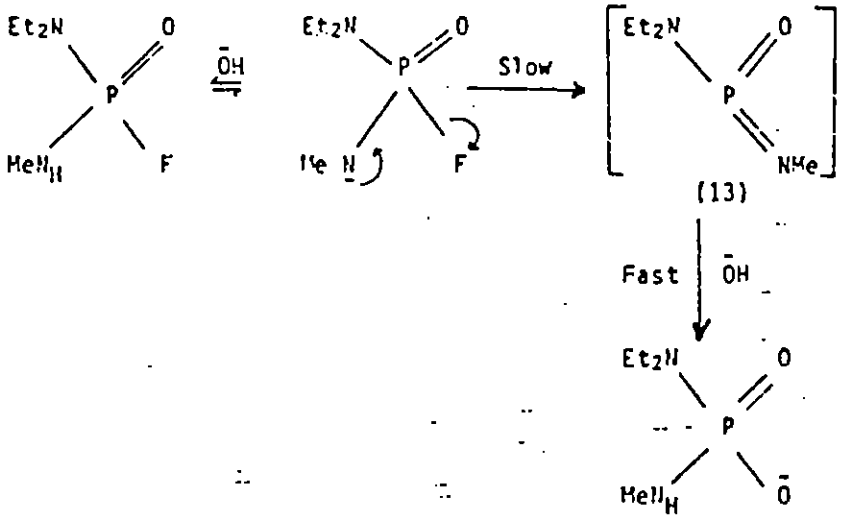


11



12

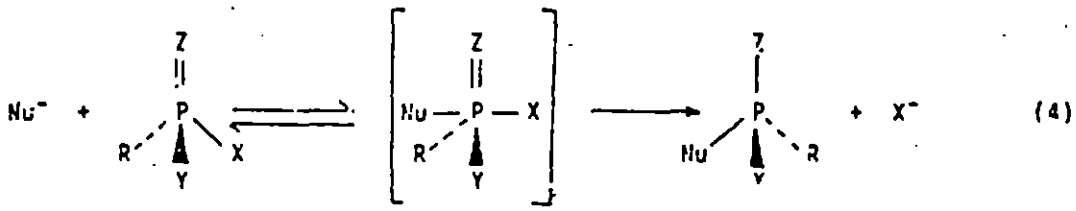
The mechanism, as written in Equation 3 involves a reactive transient intermediate, 13, a metaphosphorimidate which reacts rapidly with hydroxide ion to give products



(3)

2.2 ADDITION-ELIMINATION

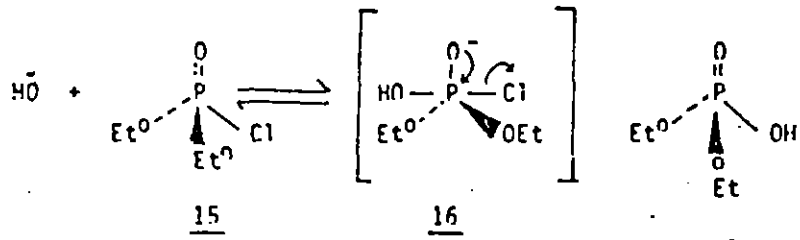
The general mechanistic scheme for addition-elimination is shown by Equation 4. It involves the formation of a pentacovalent intermediate, 14, as distinct from a transition state, and provided the nucleophile enters an apical position and the leaving group x departs from an apical position, the mechanism leads to inversion at phosphorus.



(4)

14

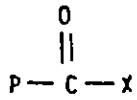
Thus, if alkaline hydrolysis of diethylphosphorochloridate, 15, occurred by addition-elimination, the mechanism would be adequately represented by Equation 5



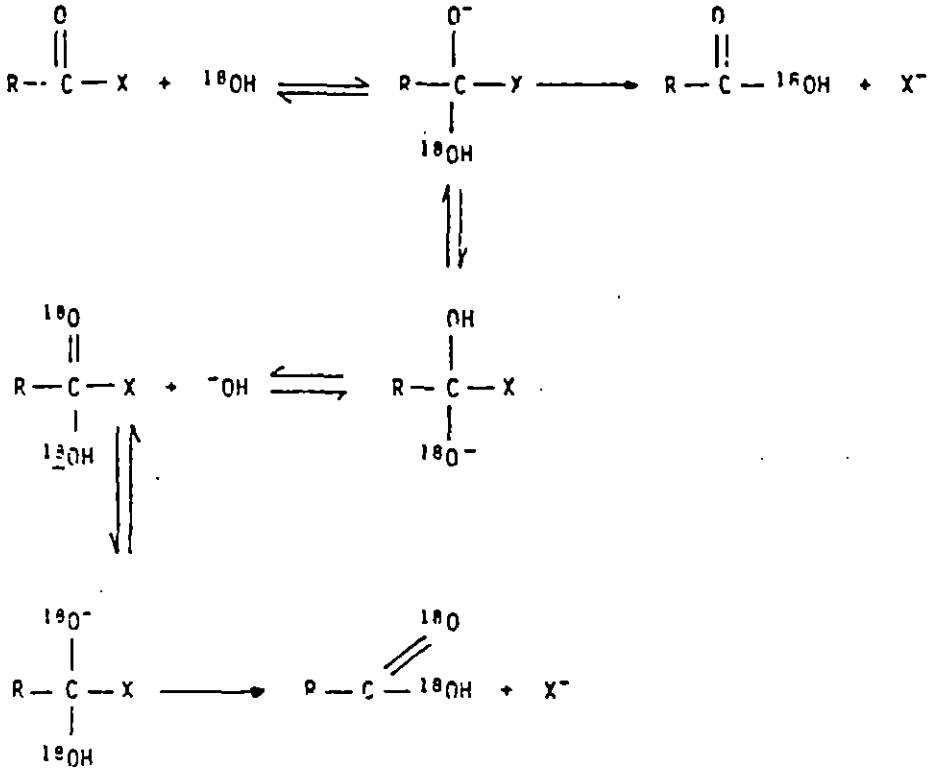
(5)

15 16

By analogy with what is known about the hydrolysis of phosphonium salts the above mechanistic scheme of Equation 5 would appear to be a reasonable guess. However, there is very little evidence to suggest that intermediates of the types 14 and 16 have any finite existence in nucleophilic displacements on acyclic phosphorus esters. The most convincing evidence in support of the above view comes from isotopic exchange studies carried out in H_2O^{18}. It is a well known fact that during the hydrolysis of carbonyl compounds like,



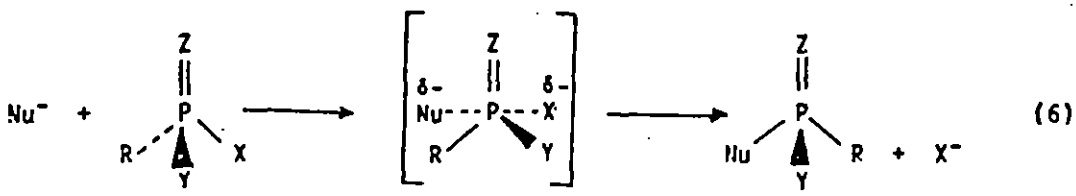
exchange occurs with the incorporation of two atoms of O^{18} in the product acid. This can only occur by reversible nucleophilic addition of hydroxide ion or water to the carbonyl compound, as shown in the scheme below:



In the hydrolysis of acylic phosphate esters,[59] phosphoryl chlorides,[60] or phosphoryl fluorides,[61] only one atom of ^{18}O is incorporated in the product acid. This provides powerful evidence to support the proposal that bond formation between the phosphorus and the nucleophile and bond cleavage between phosphorus and the leaving group is a synchronous process.

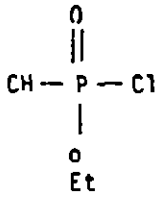
2.3 $S_N2(P)$ MECHANISM

This mechanism is directly analogous to the nucleophilic displacement at carbon and views the trigonal bipyramid of Equation 6 as a transition state rather than an intermediate.

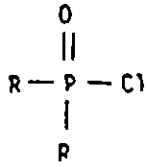


(6)

Many lines of evidence have been developed in support of the above mechanism as against the addition-elimination and it has been reviewed by Kirby and Warren.[24] Most reactions of tetrahedral phosphorus compounds with nucleophiles are first order in nucleophile and first order in phosphorous compounds. This requirement is a prerequisite of the $S_N2(P)$ mechanism but does not exclude addition elimination. These include the displacement of halide ion by amines[62,63] in Compounds 17 and 18; the displacement of halide by hydroxide[64-67] or

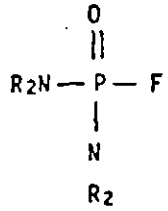


17

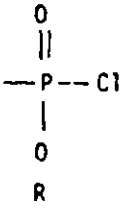


18

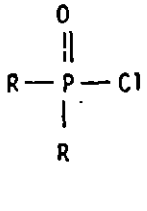
aryloxide[68] ion with Compounds 18 through 21; the



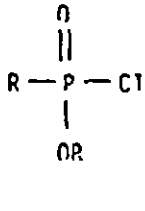
19



20

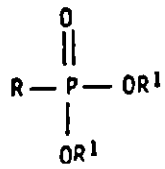


18

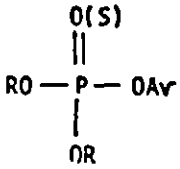


21

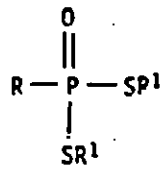
saponification of esters[69-72] and thiol esters[73] by water or hydroxide ion as in Compounds 22-24; and a



22



23

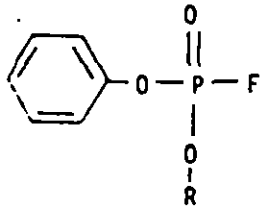


24

number of displacements by oximes,[74] fluoride,[75,76] and phosphate anions.[77,78] Where thermodynamic parameters have been measured they are consistent with a bimolecular process, the entropy of activation being large and negative. Larson quotes a number of entropy values for such reactions, ranging from -10 e.v to -31 e.v.[79] These values are more negative than the corresponding values for carbonyl compounds, contrasting the addition-elimination mechanism of displacements on carbonyl compounds with direct displacement on phosphoryl compounds.[58]

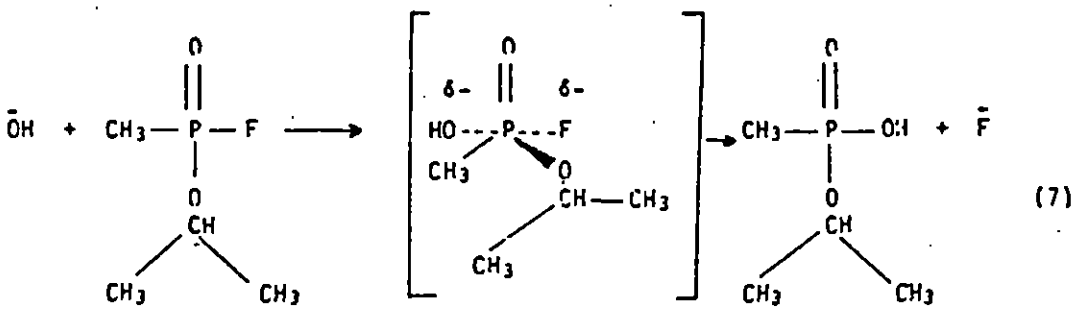
3. ALKALINE HYDROLYSIS

Perhaps the most extensively studied reaction of GB is its hydrolysis. It is not surprising therefore that the only tested demilitarization procedure for GB makes use of hydrolysis by excess sodium hydroxide. The compound is miscible with and slowly hydrolyzed by water. Arylphosphonofluoridates, 25, were reported not to hydrolyze even under heating.[80] The rate of hydrolysis



25

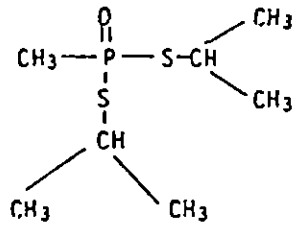
of GB increases rapidly with increasing hydroxyl ion concentration. Thus, hydrolysis by aqueous sodium hydroxide, for instance, occurs rapidly to give nontoxic products. It was seen in Section 2 of this review that alkaline hydrolysis is only a special case of the general displacement reactions of nucleophiles at tetracoordinated phosphorus. Therefore all that has been discussed under $S_N2(P)$ mechanism may be expected to hold true for the alkaline hydrolysis of GB. Accordingly, the rate of alkaline hydrolysis has been found to be directly proportional to the concentration of the ^-OH ions and is practically independent of variations of the ionic strength.[81] The low effect of the ionic strength as well as the negligible effect of the fluoride ion concentration exclude a S_N1 mechanism and support the $S_N2(P)$ mechanism discussed in Section 2.3. Alkaline hydrolysis of GB can be written, therefore, as shown in Equation 7.



(7)

From the study by Larsson[81] on the alkaline hydrolysis of GB and its analogues it was concluded that their rates of hydrolysis are controlled by the strength of the P-F bond and by the ease with which the hydroxyl ion can attack the phosphorus atom. The approach of the hydroxyl ion depends upon the electronic density of the phosphorus atom, which is controlled by the electronic effects of the substituents, and also by the steric hindrance of these substituents. The strength of the P-F bond is also influenced by the electron distribution of the substituents. The second order rate constant for GB at pH = 8.0 and temperature 25°C is calculated to be 25.8 l mole^{-1} sec^{-1}.[81] At 35°C, and pH = 9.0 the second order rate constant for alkaline hydrolysis is calculated to be 42.4 l mole^{-1} sec^{-1}.[81] The entropy of activation $\Delta S^{\neq}$ was computed to be -24 e.v.[81]

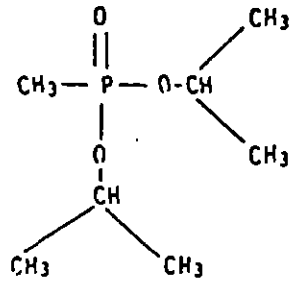
Alkaline hydrolysis of VX may be expected to follow the same mechanistic pattern as that of GB, but the rates and the bonds involved in the hydrolysis are different. VX is a thiol ester. Measurements of the rate of hydrolysis of diisopropylmethylphosphonodithiolate, 26 by estimation of the



26

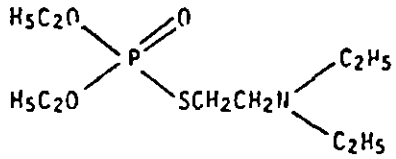
acid and thiol compound produced show that P-S bond cleavage occurs in alkaline pH and this was attributed to the low bond strength of the P-S bond,

compared to P-O bond or for that matter C-S bond.[73] The thiol ester, 26, reacts 2.5 x 10^4 times faster in alkali[73] than the corresponding oxygen ester, diisopropylmethylphosphonate, 27. Even though this reaction rate is



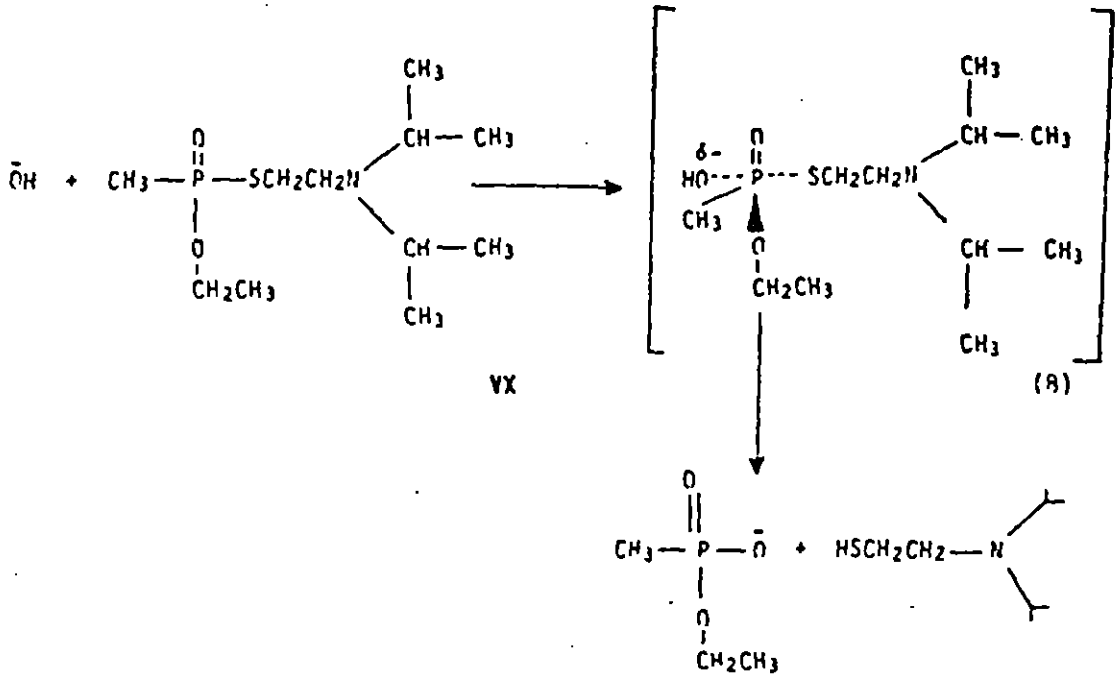
27

impressive, compared to the oxygen ester, a comparison of the rate of P-S bond cleavage (k = 2.41 l $mole^{-1}$ sec^{-1} at 25°C) with P-F bond cleavage (k ~ 25.8 l $mole^{-1}$ sec^{-1} at 25°C) shows that alkaline hydrolysis of VX is going to be much slower than that of GB under identical conditions. Fukoto and Stafford[53] showed that hydroxide ion attack on compound 28 resulted exclusively in the cleavage of the P-S bond. Along the same lines, Epstein



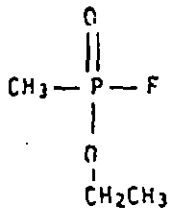
28

et al.[82] have stated that in Compound 29 and in VX exclusive cleavage of the P-S bond occurs in strongly alkaline solutions. The hydrolysis of VX in strongly alkaline solutions can therefore be written as indicated below (Equation 8).

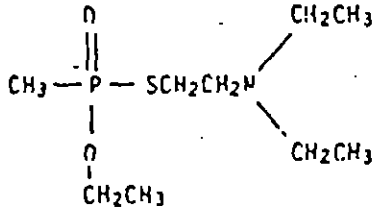


VX (8)

Besides being a thiol ester, the presence of the nitrogen in VX further complicates the hydrolysis of these compounds. A more accurate picture of the relative rates of cleavage of the P-F bond in GB versus the cleavage of P-S bond in VX can be obtained from the studies on alkaline hydrolysis of Compounds 30 and 29.



30



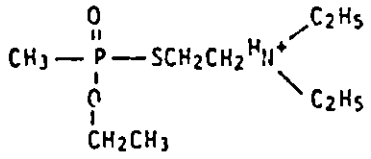
29

The bimolecular rate constants for alkaline hydrolytic cleavage of P-F bond in Compound 30 has been found by Larsson to be 60.7 M^{-1} sec^{-1}. The bimolecular rate constants for alkaline hydrolytic cleavage of P-S bond in Compound 29 has been found by Epstein et al.[82] to be 0.083 M^{-1} sec^{-1}. In other words, Compound 30 is about 7 x 10^3 times more reactive towards alkaline hydrolysis than the unprotonated form of Compound 29. If one compares the bimolecular rate constant for GB as determined by Larsson,[81] 25.8 M^{-1} sec^{-1} at 25°C, with the value quoted by Epstein for Compound 29, it is seen that GB is about 3000 times more reactive to alkaline hydrolysis than Compound 29. Therefore it is reasonable to estimate that GB would be approximately 10^3 times more reactive than unprotonated VX towards alkaline hydrolysis.

In the case of phosphonate esters the rates of hydroxide ion displacement of a particular group or atom can be correlated fairly closely with the pka of the displaced anion.[82] If the logarithm of bimolecular rate constants are plotted against the pka of the conjugate acid produced from the departing anion, a reasonably linear correlation is obtained in the case of Compound 29, in accordance with the equation

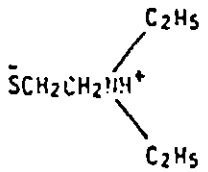
$$\ln k_2 = -0.5\ pka + 5.2$$

The significance of the above finding is that the protonated form of VX should be more susceptible to hydrolytic cleavage than the unprotonated form. In the case of Compound 29, the protonated form is shown in the structure below. The pka of the

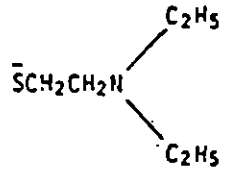


Protonated Form of 29

conjugate acid of the anion,



produced by hydrolytic cleavage of the P-S bond has been estimated as 8.25.[84] The pka of the conjugate acid of the anion,



produced by hydrolytic cleavage of the P-S bond in Compound 29 has been estimated[85] from aliphatic mercaptans of equivalent carbon number as 11. The bimolecular rate constant for alkaline cleavage of the P-S bond in Compound 29 is 0.083 M^{-1} sec^{-1} and for the protonated form of Compound 29 it is 0.39 M^{-1} sec^{-1}. The authors[82] estimate the protonated form to be 50 times as reactive as the unprotonated form. It is reasonable to expect a similar difference in reactivity between the protonated and nonprotonated forms of VX, with the protonated form being the more reactive species.

When considering alkaline hydrolysis as a process for demilitarization, other factors besides reactivity have to be considered. The enormous difference in reactivity between GB and VX towards alkaline hydrolysis has already been discussed. It was also seen that the protonated form of VX is more reactive than the unprotonated form. In addition to reactivity, the solubility of VX in strongly alkaline solution is poor whereas GB is freely miscible with the alkaline solution. The protonated form of VX has a higher solubility than the nonprotonated form in the aqueous medium, in addition to being the more reactive form. It is not unreasonable to expect GB to be at least two times more reactive than even the protonated form of VX, when alkaline hydrolysis is considered. Therefore alkaline hydrolysis, though suitable for GB demilitarization, is unsuitable for demilitarizing large quantities of VX.

Finally, this section on alkaline hydrolysis can be concluded by discussing the hydrolysis of H in aqueous solutions.

In Part I of the literature review the bonding and reactivity of H was discussed at length and it was seen that while H combines the properties of an alkyl halide and a typical sulfide, these properties are modified because of the proximity of sulfur and halogen in the molecule. The neighboring group

effect, called the anchimeric effect of sulfur, has long been known in the solvolysis of esters and halides. A characteristic example of the reactions of H as an alkyl halide would be the nucleophilic substitution of the chlorine atom by hydroxyl upon interaction with water or hydroxide ion. However, the displacement of halogen in H does not proceed as an S_N2 reaction. Peters and Walker[86] were one of the very first to study the rate of formation of acid by H in water and water-alcohol mixtures, in the presence and absence of salts, including chlorides. They worked at constant temperature and approximately constant pH and observed that the rate of reaction is independent of pH over a wide range and is strongly depressed by alcohol and is depressed by salts. Following the work of Watson[87] and Hughes,[88,89] Ogston et al.[90] interpreted these results on the basis of an S_N1 mechanism and that the rate of total reaction in aqueous solution must be unimolecular with respect to H and independent of the concentration of any substituting agent. Each of the chlorine atoms of H reacts by the S_N1 mechanism. At the very beginning of the reaction, therefore, an induction period is to be expected during which the activated form accumulates to its stationary concentration. No induction period is observed with H, at least by the detection methods used by Ogston et al., and this means that the stationary concentration of activated H must be reached in a few seconds or less. After the first replacement, the second stage of the reaction is that of a substance $YCH_2CH_2\text{-}S\text{-}CH_2CH_2Cl$ where Y is the group that has replaced chlorine in H. The reaction rate for displacing the second chlorine is likely to be different from that of the first and to depend on the nature of Y. Peters and Walker[86] observed that where Y = OH, the course of reaction is not simply unimolecular, but becomes faster as the reaction proceeds. These facts can be quantitatively accounted for on the hypothesis that the rate controlling factor in all substitutions is the S_N1 activation, followed by competing bimolecular reactions between the activated H and the substituting reagents. The mechanism put forward by Ogston[90] is as follows:

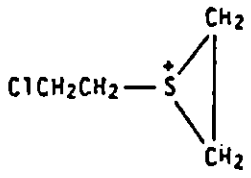
$$ClCH_2CH_2SCH_2CH_2Cl \xrightarrow{k_0} [ClCH_2CH_2SCH_2CH_2Cl]^* \qquad (9)$$

$$[ClCH_2CH_2SCH_2CH_2Cl]^* + H_2O \xrightarrow{k_1} ClCH_2CH_2SCH_2CH_2OH + HCl \qquad (10)$$

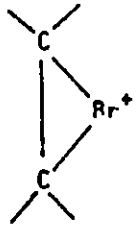
The above steps are then repeated for the subsequent displacement of chlorine. Inhibition by chloride was indicated as follows:

$$[ClCH_2CH_2SCH_2CH_2Cl]^+ + Cl^- \longrightarrow ClCH_2CH_2SCH_2CH_2Cl + Cl^- \qquad (11)$$

In the above reaction mechanism, Ogston et al[90] did not speculate on the nature of the activated form of H, $[ClCH_2CH_2SCH_2CH_2Cl]^+$. The mechanism was further clarified by Bartlett and Swain.[91] As early as 1937, Roberts and Kimball[92] had postulated the existence of ethylenebromonium ion, 31, in bromination reactions. In 1939, Weinstein and Lucas[93] demonstrated the

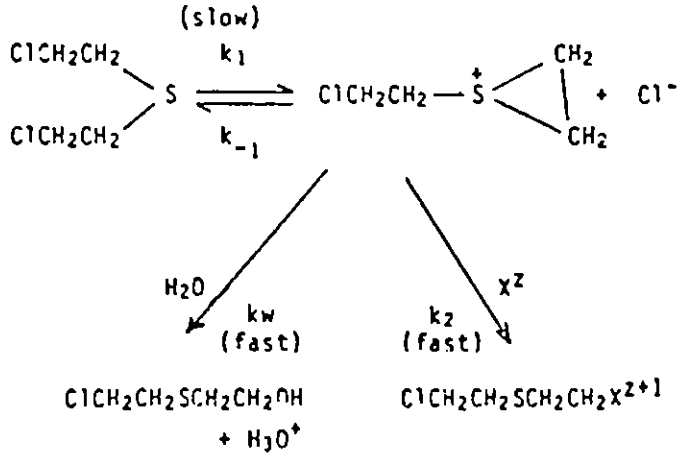


32



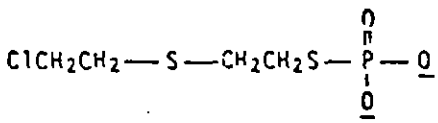
31

participation of such ions in displacement reactions of β-bromoalkyl compounds. During the second World War, it was recognized by the American workers that the closely analogous ethylenesulfonium ion, 32, offered an attractive explanation of the first order displacement reactions of H, a type of displacement kinetics not shown by any primary alkyl chloride. The mechanism could be rewritten as follows:

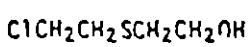


(17)

Ogston[93] et al. had posed two apparent difficulties with the above mechanism. They were: (1) that the "competition factor," defined as the ratio for any molecule or ion x capable of reacting with ethylenesulfonium ion, varied widely with the concentration of x in the case of chloride ion whereas it was expected to be constant and (2) that although, to a first approximation, the rates of reaction of H with all substances depended only upon the concentrations of H and of chloride ion, which are concerned in the first step of the mechanism, yet the initial measured first order rate constant for the reaction H with certain strong competitors such as sodium monothiophosphate was 10 percent greater than with water or weaker competition. Bartlett and Swain[91] have shown that the "competition factor" as defined above is indeed independent of chloride ion concentration if the ionic strength remains constant, but to depend upon ionic strength in a manner predictable from the Bronsted rate equation and the limiting Debye-Hückel law for the activity coefficient of an ion. Furthermore, the greater rate with strong competitors such as monothiophosphate anion compared to water has been shown to be a result of the faster cyclization of the S-2(2-chloroethylthio)-ethyl monothiophosphate ion, 33, (more than twice as fast) as compared with the chlorohydrin, 34.



33



34

While discussing the alkaline hydrolysis of VX, it was stated that an added complication to its hydrolysis relative to GB was the poor solubility of VX in aqueous alkali. The problem of aqueous solubility is even more acute when H is considered. H is heavier than water (density at 25°C is 1.2963) and is sparingly soluble (0.07% at 10°C) in water. It is readily soluble in organic solvents, fuels and lubricants. It boils at 217°C at atmospheric pressure with partial decomposition. The limited solubility in water would initally mean that at any appreciable concentration H would form a separate phase and hydrolysis would be limited by the very slow processes of diffusion and dissolution in water. This explains the possibility of prolonged existence of H under an immobile layer of water (months and even years). Nevertheless, hydrolysis in which water acts as a destructive agent was from

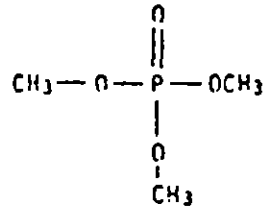
the start considered a desirable method since it is obviously simple and inexpensive if it can be made effective. The speed with which liquid H is destroyed by hydrolysis depends upon two processes: first, the rate of solution of H into the aqueous ph... and second, the rate of hydrolysis of the dissolved molecules. The fact that H hydrolyzes only after it has dissolved in the aqueous phase has been experimentally verified by showing that the rate of hydrolysis in a solution thoroughly agitated with excess H is independent of the amount of liquid H present. If the reaction took place to an appreciable extent at the interface or in the H phase, an increase in the quantity of the latter present should increase the rate of hydrolysis. In a two phase system composed of water and H, when steady conditions are maintained, a dynamic equilibrium is soon set up such that the rate of solution just equals the rate of hydrolysis and the concentration of dissolved H at a given point in the solution remains substantially constant. The time required to reach this equilibrium value is in general very small, because of the comparatively slight solubility of H in water. Therefore the rate of destruction of H by water might be accelerated by any one or combination of the following factors: (1) an increase in the specific rate of hydrolysis, i.e., an increase in the rate constant for the slow step shown in Equation 12, (2) an increase in the solubility of H in water phase, (3) an increase in the rate of dissolution of H in water, and (4) finally an increase in the area of interface.

The effect of alkaline colloidal agents on the above factors has been studied by Wilson, Fuller, and Schur.[94] They found that solutions such as those of alkaline sulfonated corn oil had no tendency to increase the specific rate of hydrolysis, nor the solubility of mustard gas in the aqueous phase. The colloidal oil particles did tend to dissolve mustard gas from the aqueous phase and thereby decrease the effective rate of hydrolysis in a solution initially saturated with mustard gas, but containing no excess liquid phase. However, it was found that the alkaline colloidal solutions did accelerate the specific rate of solution per unit area of interface by acting as carriers to transport mustard gas from the very thin aqueous layer through which it was diffusing before hydrolysis was complete. The action was especially effective in the case of moderately alkaline sulfonated corn oil solutions, where the acid released by hydrolysis in the film near the mustard gas surface precipitated oil globules therein, which rapidly dissolved a large amount of

mustard gas and were then carried up by circulation currents into the main body of solution where they redissolved and released the mustard gas in such form that it was very rapidly hydrolyzed.

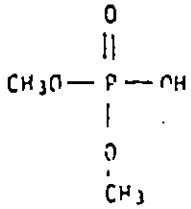
4. ACID HYDROLYSIS

The hydrolysis of trimethylphosphate, 35, in acidic solution is slow and is not acid catalyzed.[95,96] The reaction is subject to a significant salt

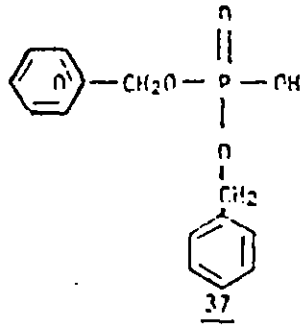


35

effect. It probably involves S_N2 attack by water on carbon in agreement with exclusive C-O fission.[97] In this way phosphates resemble sulfonate esters which, however, are considerably more reactive. Dimethylphosphate, 36 and dibenzylphosphate, 37 are however acid catalyzed, the rate increasing linearly with acid concentration in solutions of constant ionic strengths. The neutral species reacts with ~20-30% P-O fission,[97] the acid catalyzed



36

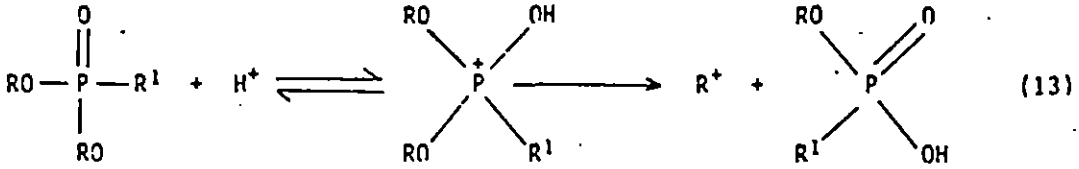


37

reaction giving almost exclusively C-O fission. The two independent investigators give 11% P-O fission[97] and ~0% P-O fission.[98]

Similarly the hydrolysis of phosphonate esters is acid catalyzed,[63] as they are more basic than phosphates. Approximately a ten-fold rate increase

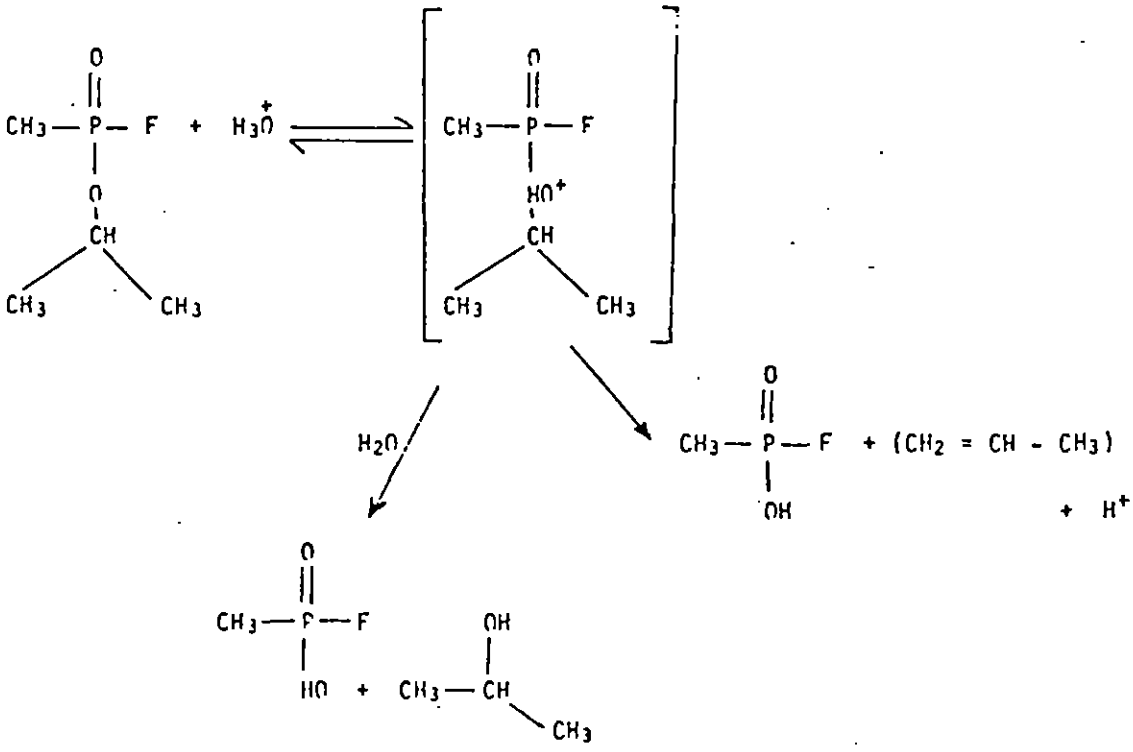
is observed in 1N benzene sulfonic acid as one goes from phosphate esters to phosphonate esters. The rate sequence Me > Et < i-Pr << t-Bu suggests that secondary and tertiary esters (tert-butyl ester hydrolyzes spontaneously at room temp)[99] react by an S_N1 mechanism as shown below (Equation 13).



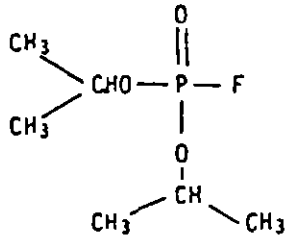
(13)

This mechanism is supported by a complete racemisation of the secondary alcohols[100] released in the reaction, and by the formation of high yields of isoamylene in the hydrolysis of neopentyl phosphonate.[69] The complete racemization of the secondary alcohol suggests that a free secondary carbonium ion is formed.

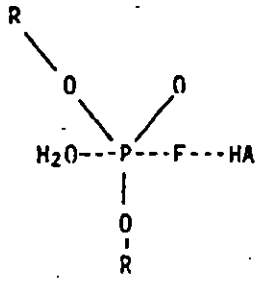
On the basis of the above discussion one might expect the following mechanism for the acid hydrolysis of GB.



However, a study has been made on the possibility of oxygen exchange between water and the phosphoryl group of diisopropyl phosphonofluoridate, 3R, on hydrolysis in H_2O.[18] No oxygen[18] exchange was found, proving that the addition of water to the phosphoryl group cannot be a preliminary fast and reversible step.[101,102] A termolecular push-pull-mechanism via a penta-coordinated intermediate, has been proposed, the rate determining (where HA is

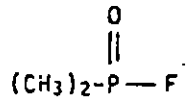


3R



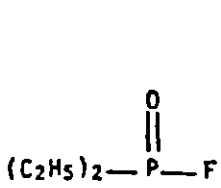
39

acid catalyst) step involving both proton transfer and nucleophilic attack.[101,102] In the same manner, the hydrolysis of



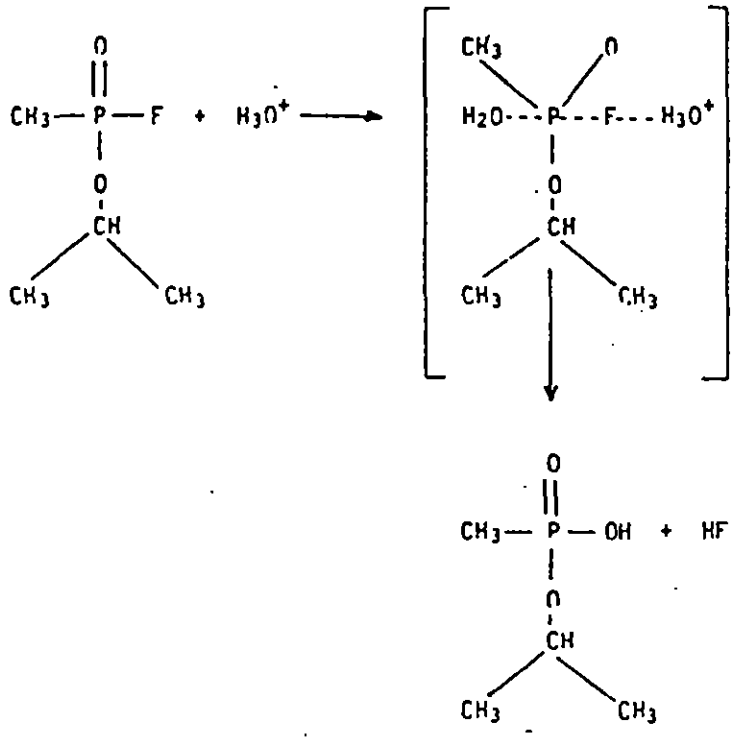
40

is acid catalyzed.[101,102] Once again there is no appreciable oxygen-exchange during the hydrolysis of dimethylphosphinic fluoride, 40, and the addition of water does not seem to be a preliminary first and reversible step. A termolecular "push-pull" mechanism has been proposed to account for the experimental observations. This involves the following trigonal bipyramidal transition state (Sp3-d hybrid) which is also suggested by displacement reactions on optically active phosphorus compounds.[103] The rate determining step in the hydrolysis thus seems to involve both proton transfer and nucleophilic attack. The acid hydrolysis of



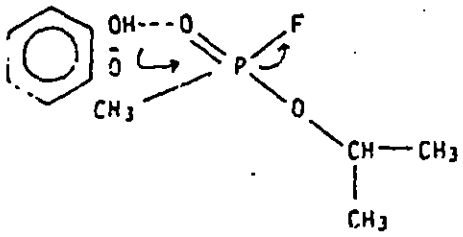
41

has also been studied[104] giving results in agreement with what was said above. On the basis of these observations, the acid hydrolysis of GB may be expected to proceed as follows.

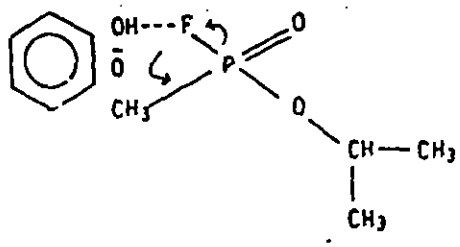


(15)

In other words, it is the P-F bond that is broken in the above mechanism, whereas it is the O-C bond that is broken if the mechanism shown in Equation 14 is correct. General acid catalysis is revealed by $k_{D_2O}/k_{H_2O} > 1$ in some solvolyses. Intramolecular general acid catalysis has been detected in some phosphate hydrolyses. The catechol monoanion reacts more quickly with GB than does phenoxide ion, presumably by general acid catalysis at the phosphonyl oxygen or fluorine atoms,[105-107] as shown below.

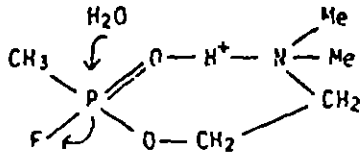


42



43

A corresponding reaction in the aliphatic series may occur during the hydrolysis of the phosphonofluoridate, 44, which is too fast to measure in slightly acidic solution when the nitrogen atom is protonated.[108,109]



44

Unlike in the case of GB, hydrolysis of VX is not catalyzed by moderately acid solutions. However, the protonation of the nitrogen atom in VX might improve the solubility of VX in acidic solutions. In the case of H, the hydrolysis is suppressed when the solution is made acidic.

5. HYDROLYSIS IN NEUTRAL SOLUTION

The work of Heath[64] has shown that the hydrolysis of organophosphate esters in water is consistent with water acting as an anionoid reagent. In the case of GB, in unbuffered solutions it is very difficult to measure the uncatalyzed rate. Because the acid produced initially acts as autocatalysis to further accelerate the hydrolysis. The overall hydrolysis constant in neutral solution is made up of five terms.

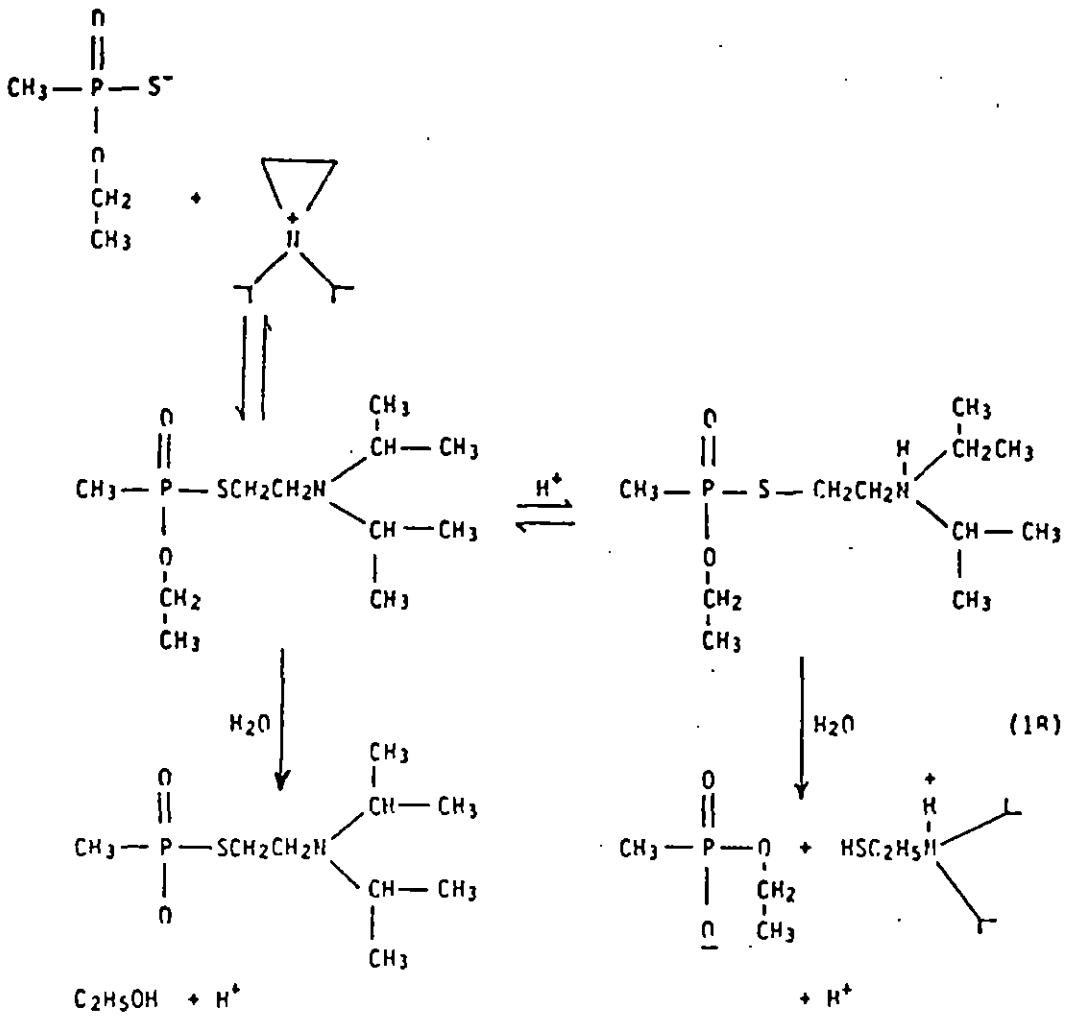
$$k = k_w + k_H [H^+] + k_{OH^-} [OH^-] + k_A [A] + k_B [B] \qquad (16)$$

k_B and k_A are constants for the catalysis by general bases and acids respectively. Kilpatrick and Kilpatrick[110] in their study of the hydrolysis of diisopropylphosphorofluoridate, 38, have shown that k_B and k_A are much greater than k_w.

In the case of VX, in neutral conditions, products from the simultaneous cleavage of P-S, O-C, and C-S bonds are observed.[87] The first order rate constant at any pH can be calculated from Equation 17, consisting of contributions from three individual rates, viz.,

$$k_{OH} = k_{H_2O} \frac{[H^+]}{k_a + [H^+]} + k \frac{k_a}{K_a + [H^+]} + k_{OH} [^-OH] \frac{k_a}{k_a + [H^+]} \qquad (17)$$

k_{H_2O} and k are first-order rate constants and k_{OH} is a second-order rate constant for the reaction between the unprotonated VX and hydroxide ion. The term $k\ k_a/k_a + [H^+]$ is the dominant term at neutral pH and represents the kinetics of the reactions proceeding with simultaneous cleavage of the P-S, O-C and S-C bonds in VX. The predominant reactions are as indicated below. Even though the overall rates are low, the different rates are of comparable



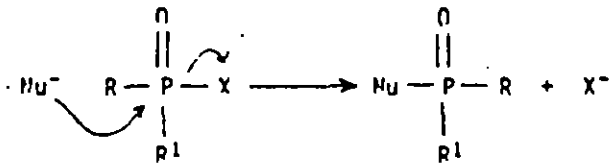
(1R)

magnitude and therefore the product distribution is complex in the case of VX. In the case of H, there is no change from what was discussed under alkaline hydrolysis.

6. CATALYSIS

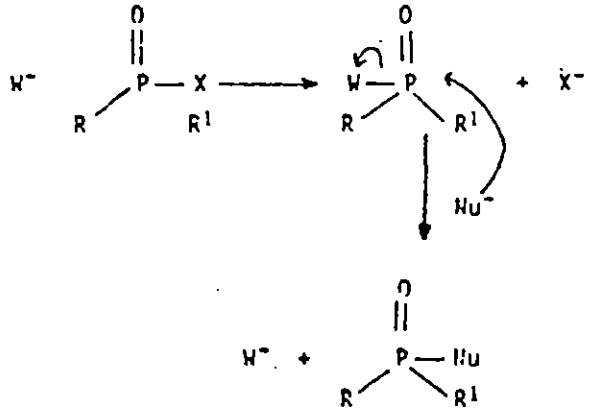
A large amount of work has been done in the study of different nucleophiles involved in accelerating the hydrolytic rates. If a nucleophile is to be a catalyst, both the displacement of the leaving group to form an intermediate and the displacement of the catalyst by the nucleophile it is assisting must be faster than the uncatalyzed reaction. The catalyst must therefore possess qualities of a nucleophile and a leaving group. Thus:

Uncatalyzed reaction



(19)

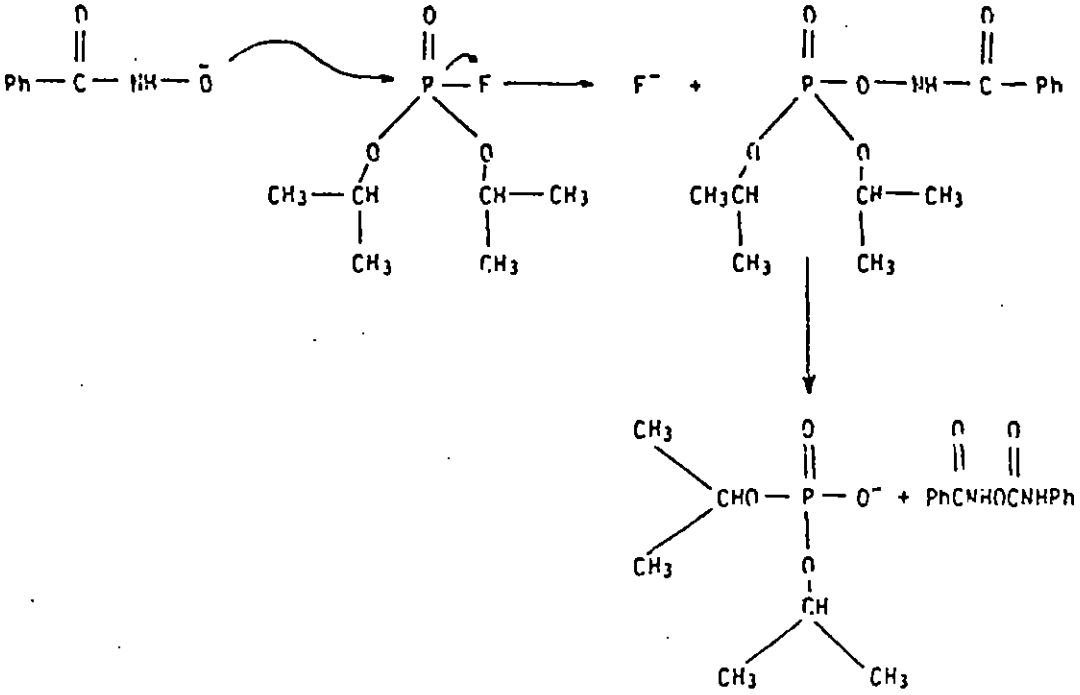
Catalyzed reaction (W = catalyst)



(20)

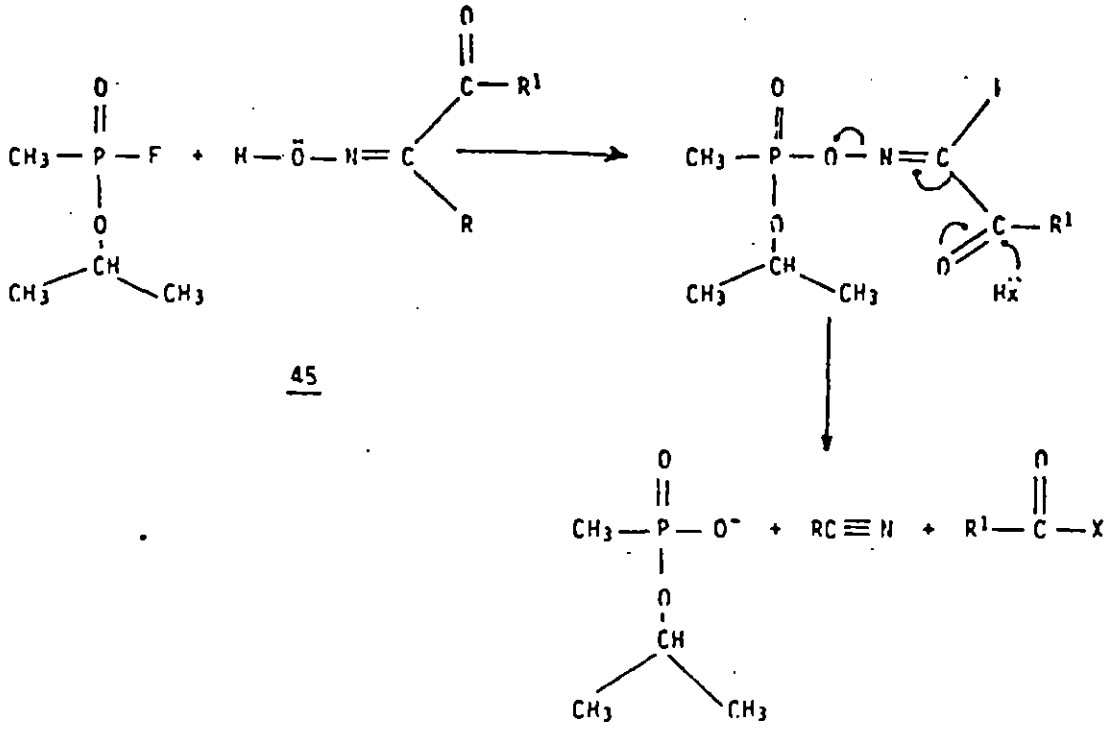
Exceptions to this principle do occur when the intermediate decomposes in some other way than by nucleophilic attack of Nu^-. The process is not then strictly catalysis, since catalyst is not regenerated. For example, the

hydrolysis of DFP, 38, is accelerated at pH 6 many hundred fold at room temperature by hydroxamic acids. These compounds are better nucleophiles for phosphorus than their basicity would suggest and thus fulfill the first requirement for nucleophilic catalysis.[111-113] They are however not a good leaving group and the intermediate has been shown to decompose by a Lossen rearrangement,[113] the products being diisopropylphosphate and a carbamate.



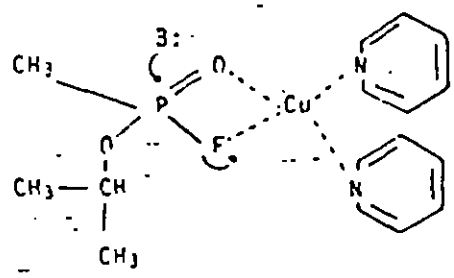
(21)

The kinetics of the accelerated reaction are consistent with a rate determining nucleophilic attack by the hydroxamic acid on DFP, the reaction being first order in the hydroxamic acid and in DFP.[74,114] Oximes also effectively accelerate the hydrolysis of GB and various phosphorochloridates. When GB is hydrolyzed in the presence of the oxime, 45, the products are isopropylmethylphosphonate, fluoride, nitrite and carboxylic acid. If aniline is added into the reaction vessel, it is acylated. The mechanism is presumably what is shown in Equation 22.



45 (22)

Similar reactions occur with nucleophiles known to show the so-called α-effect, hypochlorite ion,[116,117] peroxide ion, and hydroxylamine.[118] Intramolecular general acid catalysis was already discussed in the context of acid hydrolysis in Section 4. Metal ion catalysis of nucleophilic attack at phosphorus is probably due to electron withdrawal from the phosphorus atom following formation of a complex with metal ion by both the leaving group and the P = O bond as shown in 46.



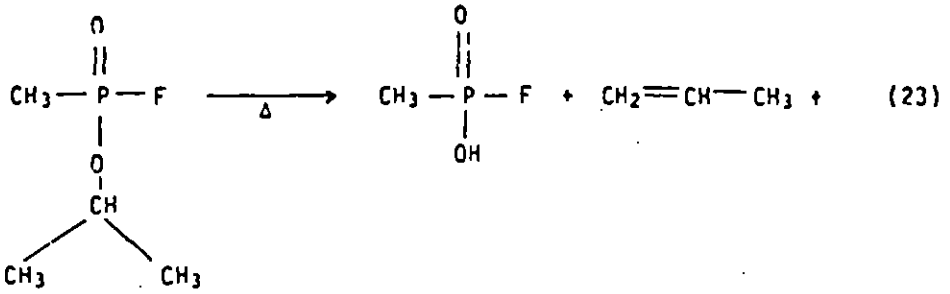
46

DFP and GB are hydrolyzed quickly in the presence of Cu (II) dipyridyl complexes, presumably by 46.[119-121] U (VI), Zr (VI), Th (IV), and Mo (VI) are also effective catalysts. Lanthanum hydroxide gels have also been shown to catalyze the hydrolysis of a number of phosphate esters near pH 8.[122]

Similar studies have not been done in the case of VX and these considerations are not applicable to the hydrolysis of H'agents. However a number of these catalysts were studied in connection with the decontamination of G-agents.

7. PYROLYSIS

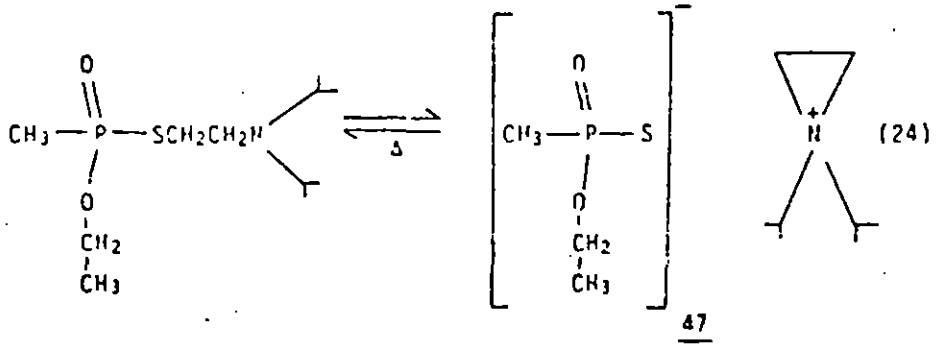
All three agents, H', G', and V can be pyrolyzed. GB can be pyrolyzed at low temperatures (~150°C) and only methyl phosphonofluoridic acid and propylene are produced.[123] The reaction can be written as follows.



(23)

The reaction has been studied in flow trains at atmospheric pressure and in the temperature range of 333° to 400°C.[124]

Pyrolysis of VX does not proceed as cleanly as does GB. In the case of VX, the S-C bond cleavage becomes the predominant mode of decomposition at higher temperatures.[82,125] On this basis the following reactions may be written for the pyrolysis of VX.

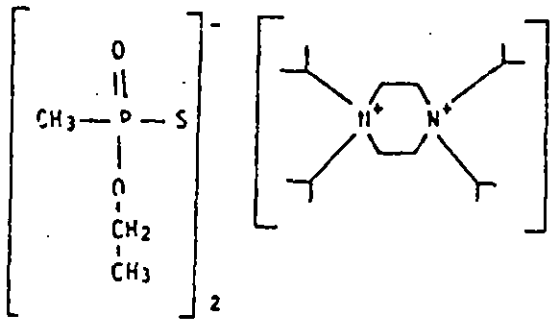


47

(24)

In the case of GB, one of the products of decomposition is propylene which is removed from the system. However, the ethyleneimonium ion cannot be removed in a similar manner and a number of side reactions of this reactive species is possible, especially in concentrated solutions. First of all the high

nucleophilicity of thiophosphonate ions for mustard type cations[126] would mean that the equilibrium lies far to the left at lower temperatures. In addition, at higher temperatures the mustard type cation might dimerize or polymerize, giving rise to products such as 48. In any case



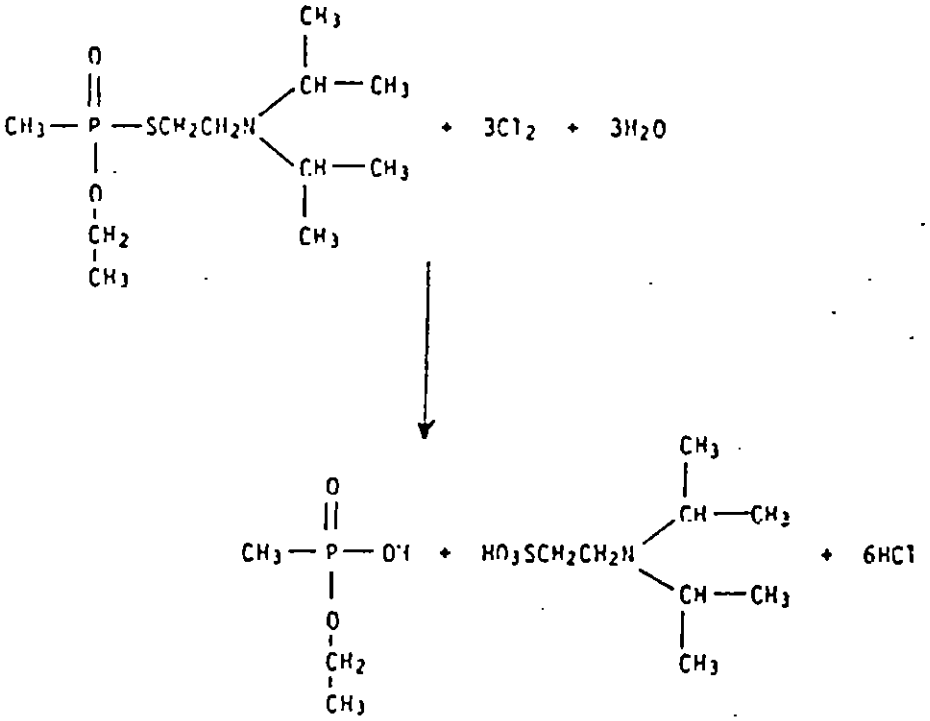
48

the products from VX pyrolysis are expected to be complex.

Pyrolysis of H'agents at lower temperatures would give polymeric materials in addition to vinylchloride, H_2S, HCl, and so on. As long as these polymeric materials have a certain amount of chlorine left in them, one should suspect these halogens to be present as β-haloethane type, the halogen being β to the sulfide sulfur and therefore they may be expected to be toxic vessicants.

8. CHLORINATION

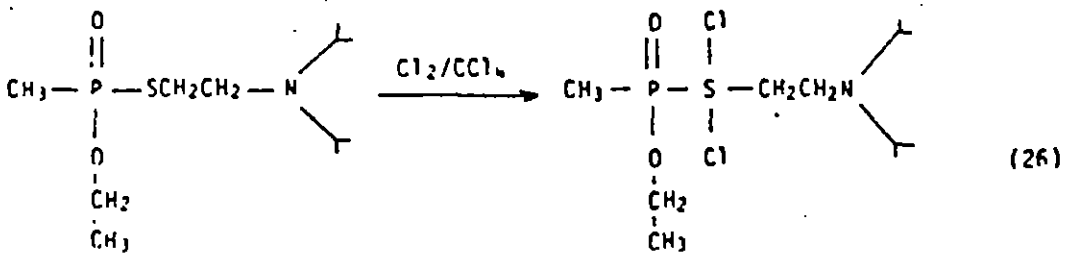
It was seen under the discussion on catalysis (Section 6) that hypochlorite anions catalyze the decomposition of G agents many times faster than their basicity would suggest. In dilute solutions aqueous chlorinolysis of H agents are possible to give eventually the fully oxidized fragments. V agents contain two sites that are exceptionally suitable for potential oxidative destruction, a sulfur and a nitrogen atom. Aqueous chlorination has been widely employed for the decontamination of VX. At pH ~ 4, the detoxification of dilute aqueous solution of VX is related solely to formation of chlorine and is independent of VX concentration. The equation summarizing reactants and products is as follows.[127]



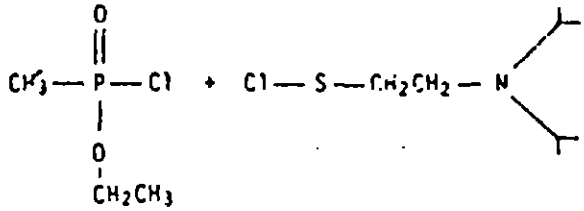
(25)

In this section the reaction of Cl_2 and other chlorinating agents like thionyl chloride and phosgene on the three agents will be discussed. Under non-

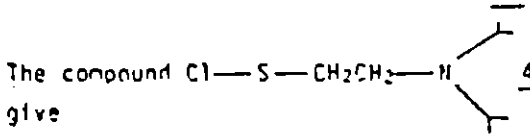
aqueous conditions the chlorination of VX is expected to proceed as written below:

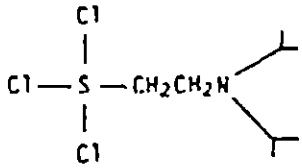


(26)



51

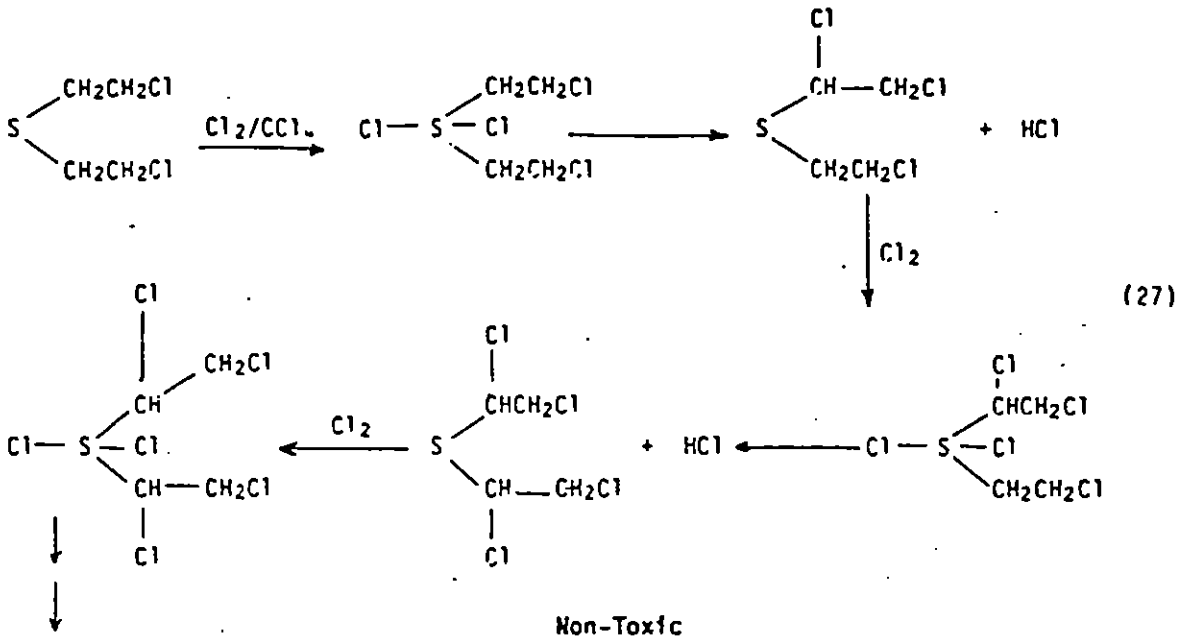
The compound  49 would futher react with chlorine to give



50

and so on. The interest in non-aqueous chlorinolysis of VX is in the fact that the oethyl-methyl-phosphono-chloridate, 51, formed is a reactive intermediate for further transformations into compounds that may eventually find use in military or industry.

The non aqueous chlorinolysis of H'agents could be expected to proceed as follows:

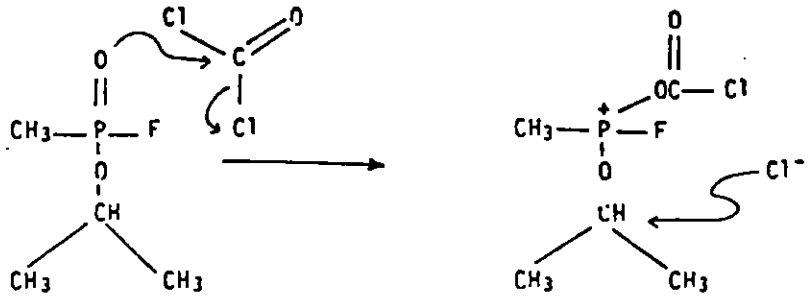


(27)

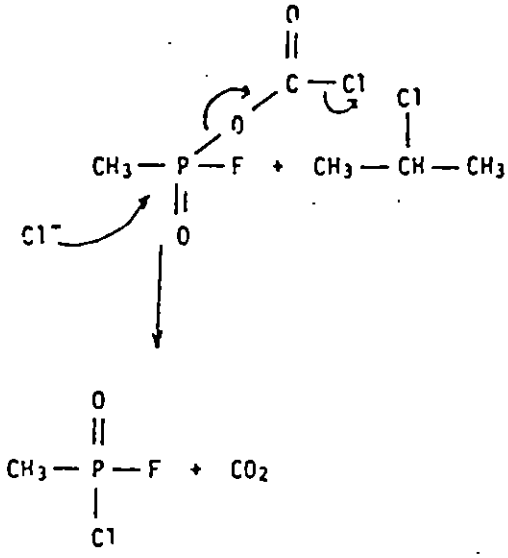
Non-Toxic

and so on until CCl_3CH_2Cl and S_2Cl_2 are formed.

Direct chlorination of GB would not be possible, as was the case with H' and V' agents which contain sulfur in their molecules. However, several chlorinating agents, thionyl chloride, phosphorus pentachloride, and phosgene convert phosphorus esters into the corresponding chlorides. In particular carbonyl chloride removes one ester group only in a clean reaction to give the phosphonochloridate from the corresponding phosphonate.[128] The mechanism of these reactions has been studied by Green and Hudson'[29] and also by Cadogan.[130] The phosphoryl oxygen atom - P = O shows little of the nucleophilicity of the - P = C or - P = N groups. But under vigorous conditions reactions do occur. It seems clear that the reaction occurs by a succession of nucleophilic displacements as shown below:



(28)



Similar mechanisms can be written for reaction of phosphonates with thionyl chloride or PCl_5. Most of these reactions are carried out with phosphonate esters and very little if any information exist on the reaction of these chlorinating agents with GB or VX.

9. CONCLUSION

This section of the literature review looks at some of the reactions of GB, VX, and H on the basis of considerations already discussed in Part 1. Hydrolysis, pyrolysis, and chlorination have been discussed in detail. There are several reactions which were not covered because the paucity of information would not lend itself to any detailed discussion. One such reaction is the reduction of phosphonates or phosphonochloridates to phosphines. The present information on these reactions does not warrant any detailed chemical engineering evaluation of these reactions. In all these discussions the chemistry of chemically pure agents is discussed. How the chemistry would go when impure agents are used cannot be predicted at this point. The bulk of the literature is on hydrolysis. However it is clear from the discussion above that one could equally well exploit the nonaqueous chemistry. The major hurdle for H and V agents is their relative water insolubility. Such problems are circumvented by working in nonaqueous media.

REFERENCES

1. McCombie, H. and Saunders, B.C., Nature, 157, 287 (1946).

2. McCombie, H. and Saunders, B.C., Nature, 157, 776 (1946).

3. McCombie, H., Saunders, B.C., and Stacey, G.J., *J. Chem. Soc.*, 921 (1945).

4. Davies, N. and Dick, J.H., *J. Chem. Soc.*, 483 (1932).

5. Schrader, G., BIOS Final Report, 1095 (1946).

6. Schrader, G., Bayer, O., and Kukenthal, H., (Farbenfabriken Bayer, A.G.): D.R.P., 664.062 (1935/38).

7. David, W.A. and Kilby, B.A., *Nature*, 164, 522 (1949).

8. Gardiner, J.E. and Kilby, B.A., *J. Chem. Soc.*, 1769 (1950).

9. Michaelis, A., *Liebigs Ann. Chem.*, 326, 172 (1906).

10. Michaelis, A. and Luxembourg, K., *Ber.*, 29, 710 (1896).

11. Schrader, G. (Farbenfabriken Bayer, A.G.): D.B.P., 767.511 (1937/52).

12. Schrader, G., Gebhardt, H., (Farbenfabriken Bayer, A.G.): D.B.P. 767.830 (1939/1953)

13. Schrader, G. and Kukenthal, H., (Farbenfabriken Bayer, A.G.) D.B.P. 767.723 (1937/52).

14. Collomp: Les Trilons, *Bull. Inf. Scient. Min. Guerre* (Sect. Techn. de l'Armee) Paris, 1949, No. 23 G, 1.

15. Lohs, K.J., Synthethische Gifte 3rd Ed., p. 190, 204, 248 Berlin: Deutscher Militareurlag (1957).

16. Saunders, B.C., "Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine," p. 91, Cambridge (Great Britain) Cambridge University Press, 1957.

17. Adrian, E.D., Feldberg, W., and Kilby, B.A., *Brit. J. Pharmacol.* 2, 56 (1947).

18. Kabachnik, M.E., Brestkin, A.P., and Michelson, M.J.; 9th Mendeleev Meeting of General and Applied Chemistry; Nauka, Moscow (1956).

19. Michelson, M.J. and Zeimal', E.V., "Acetylcholine: An Approach to the Molecular Mechanism of Action," Translated from the Russian by E. Lesser and M. Lesser; pergamon Press (1973).

20. Tammelin, L.E. and Enander, I., Proc. Intern. Congr. Biochem., 4th Congr., Vienna, Abstr. 4-10 (1948).

21. De Clermont, Ph., *Compt. Rend.*, 39, 338 (1854).

22. Cramer, F. and Hettler, H., *Chem. Ber.*, 91, 1181 (1958).

23. Hudson, R.F., "Structure and Mechanism in Organophosphorus Chemistry," London-New York; Academic Press, 1965.

24. Kirby, A.J. and Warren, S.G., "The Organic Chemistry of Phosphorus," Amsterdam-London-New York; Elsevier Publishing Company (1967).

25. Gier, T.E., *J. Am. Chem. Soc.*, 83, 1769 (1961).

26. Pitzer, K.S., *J. Am. Chem. Soc.*, 70, 2140 (1948).

27. Mulliken, R.S., *J. Am. Chem. Soc.*, 72, 4493 (1950).

28. Paetzold, R., *Z. Chem.*, 4, 321 (1964).

29. Gianturco, F.A., *J. Chem. Soc.*, (A), 1293 (1969).

30. Jolly, W.L., *Inorg. Chem.*, 3, 459 (1964).

31. Remy, H., Treatise on Inorganic Chemistry Vol. 1, 75 (1956); Elsevier, New York.

32. Sheppard, W.A. and Sharts, C.M., Organic Fluorine Chemistry, p. 16 (1969) W.A. Benjamin Inc., New York.

33. Pauling, L., "The Nature of the Chemical Bond," 3rd Ed., Ithaca, New York, Cornell University Press 1960.

34. Van Wazer, J.R., Phosphorus and its compounds Vol. I and II. New York London; Inter-science Publishers Inc. (1958).

35. Selim, M. and Thank, T.N., *Compt. Rend.*, 250, 2377 (1960).

36. Sayre, R., *J. Am. Chem. Soc.*, 80, 5438 (1958).

37. Gillis, R.G., Horwood, J.F. and White, G.L., *J. Am. Chem. Soc.*, 80, 2999 (1958).

38. Lucken, E.A. and Whitehead, M.A., *J. Chem. Soc.*, 2459 (1961).

39. Cruickshank, D.W., Webster, R.C., and Mayers, D.F., *J. Chem. Phys.*, 40, 3733 (1964).

40. Collin, R.L., *J. Am. Chem. Soc.*, 88, 3281 (1966).

41. Cox, J.R. and Ramsay, O.B., *Chem. Rev.*, 317 (1964).

42. Craig, Maccoll, Nyholm, Orgel, and Sutton, *J. Chem. Soc.*, 332 (1954).

43. Craig, Maccoll, Nyholm, Orgel, and Sutton, *J. Chem. Soc.*, 354 (1954).

44. Bissey, J.E., *J. Chem. Educ.*, 44, 95 (1967).

45. Goubeau, J. *Angew. Chem. Int. Ed.*, 8, 328 (1969).

46. Ref. 34, Vol, Page 360.

47. Kabachnik, M.I., *Z. Chem.*, 2, 289 (1961).

48. Conant, J.B. and Cook, A.A., *J. Am. Chem. Soc.*, 52, 830 (1920).

49. Meister, A. and Swan, J.M., *Australian J. Chem.*, 16, 725 (1963).

50. Gillespie, R.J., *J. Chem. Soc.*, 1002 (1952).

51. Craig, D.P. and Zauli, C., *J. Chem. Phys.*, 37 601, 609 (1962).

52. Fest, C. and Schmidt, K.J., "The Chemistry of Organophosphorus Pesticides," Springer-Verlag Berlin Heidelberg New York page 63 (1973).

53. Fukuto, T.R. and Stafford, E.M., *J. Am. Chem. Soc.*, 79, 6083 (1957).

54. Fukuto, T.R. and Metcalf, R.L., *J. Am. Chem. Soc.*, 76, 5103 (1954).

55. Literature Review - Part 1, of this appendix.

56. Hoffmann, A.W., *Ber*, 6, 303 (1873).

57. Michaelis, A and Wenner, F., *Ber*, 48, 316, (1915).

58. Aksnes, G. and Songstad, J., *Acta. Chem. Scand.*, 19, 893, (1965).

59. Samuel, D and Silver, B.L., in Gold, v(Ed), Advances in Physical Organic Chemistry, Vol. 3, page 123. Academic Press, New York, 1965.

60. Dostrovsky, I. and Halmann, M., *J. Chem. Soc.*, 1004, (1956).

61. Halmann, M., *J. Chem. Soc.*, 305, (1959).

62. Keay, L., *J. Org. Chem.*, 28, 329, (1963).

63. Dostrovsky, I. and Halmann, M., *J. Chem. Soc.*, 511 (1953).

64. Heath, D.F., *J. Chem. Soc.*, 3804, (1956).

65. Hudson, R.F., and Keay, L., *J. Chem. Soc.*, 1859, (1960).

66. Devonshire, L.N. and Rowley, H.H., *Inorg. Chem.*, 1, 680, (1962).

67. Hudson, R.F. and Moss, G., *J. Chem. Soc.*, 1040, (1964).

68. Epstein, J., Plapinger, R.E., Michel, H.O., Cable, J.R., Stephani, J.P., Hester, R.J., Billington, C., and List, G.R., *J. Am. Chem. Soc.*, 86, 3075, (1964).

69. Hudson, R.F. and Keay, L., *J. Chem. Soc.* 2463, (1956).

70. Coult, D.A. and Green, M., *J. Chem. Soc.* 5478, (1964).

71. Hudson, R.F., *Ann. Chim.* (Italy) 53, 47, (1963).

72. Ketelaar, J.A.A., Gersmann, H.R., and Koopmans, K., *Rec. Trav. Chim.*, 71, 1253, (1952).

73. Hudson, R.F. and Keay, L., *J. Chem. Soc.*, 3269, (1956).

74. Green, A.L., Sainsbury, G., Saville, B. and Stansfield, M., *J. Chem. Soc.*, 1583, (1958).

75. Dostrovsky, I., and Halmann, M., *J. Chem. Soc.*, 508, (1953).

76. Park, J.H. and Koshland, D.E., *J. Biol. Chem.*, 233, 986, (1958).

77. Hamer, N.K., *J. Chem. Soc.*, 46, (1965).

78. Clark, V.M., and Warren, S.G., *J. Chem. Soc.*, 5509, (1965).

79. Larsson, L., *Svensk. Kem. Tidsk.*, 70, 405, (1958).

80. Yanupol'skii, L.M. and Ivanova, Zh.M., *Zh. Obshch. Khim.*, 30, 1284, (1960).

81. Larsson, L., *Acta. Chem. Scand.*, 11, 1131, (1957).

82. Epstein, J., Callahan, J.J., and Bauer, V.E., *Phosphorus*, 4, 157, (1974).

83. Larsson, L., *Acta. Chem. Scand.*, 12, 723, (1958).

84. Ref. 82, Quoted as Personal Communication From MARSH, D.L.

85. Arnett, E.M., "Progress in Physical Organic Chemistry," Vol. 1, p. 391, Interscience Publishers, New York, N.Y., 1963.

86. Peters, R.A. Walker, E., *Biochem. J.*, 17, 260, (1923).

87. Watson, *Ann. Reports*, 208, (1938).

88. Hughes, *J. Chem. Soc.*, 255 (1935).

89. Hughes, *J. Chem. Soc.*, 1183, (1937).

90. Ogston, A.G., Holliday, E.R., Philpot, J. St. L., and Stocken, L. A., Transactions of the Faraday Society, 44, 45, (1948).

91. Bartlett, P.D., and Swain, C.G., *J. Am. Chem. Soc.*, 71, 1406, (1949).

92. Roberts, I. and Kimball, G.E., *J. Am. Chem. Soc.*, 59, 947, (1937).

93. Winstein, S., and Lucas, H.J., *J. Am. Chem. Soc.*, 61, 1576, 1581, and 2845 (1939).

94. Wilson, P.E., Fuller, E.W., and Schur, M.O., *J. Chem. Soc.*, 2762, (1922).

95. Barnard, P.W.C., Bunton, C.A., Llewellyn, D.R., Vernon, C.A., and Welch, V.A., *J. Chem. Soc.*, 2670, (1961).

96. Vernon, C.A., *Chem. Soc. Spec. Publ.*, 8, 17, (1957).

97. Bunton, C.A., Mhala, M.M., Oldham, K.G., and Vernon, C.A., *J. Chem. Soc.*, 3293, (1960).

98. Haake, P.C. and Westheimer, F.H., *J. Amer. Chem. Soc.*, 83, 1102, (1961).

99. Cox, J.R. and Westheimer, F.H., *J. Amer. Chem, Soc.*, 80, 5442, (1958).

100. Gerrard, W., Green, W.J., and Watkins, R.A., *J. Chem. Soc.*, 4076, (1952) and Keay, L., *J. Org. Chem.*, 28, 1426, (1963).

101. Halmann, M., *Bull. Res. Coun.*, Israel, 7A, Sept. 1958, No. 4.

102. Halmann, M., *J. Chem. Soc.*, 305, (1959).

103. Green, M. and Hudson, R.F., *Proc. Chem. Soc.*, 227, (1959).

104. Aksnes, G. and Snarrud, S.I., *Acta. Chem. Scand.*, 15, 457, (1961).

105. Sandorf, B.J., Wagner-Jauregg, T., O'Neill, J.J. and Stolberg, M.A., *J. Amer. Chem. Soc.*, 74, 1521, (1952).

106. Augustinson, K.B., *Acta. Chem. Scand.*, 6, 959, (1952).

107. Epstein, J., Rosenblatt, D.H., and Denek, M.M., *J. Am. Chem. Soc.*, 78, 341, (1956).

108. Tommelin, L.E., *Acta. Chem. Scand.*, 11, 859 (1957).

109. Larsson, L., *Acta. Chem. Scand.*, 12, 587, (1958).

110. Kilpatrick and Kilpatrick, *J. Phys. Colloid. Chem.*, 53, 1371, (1949).

111. Hackley, B.E., Plazinger, R., Stolberg, M., and Wagner-Jauregg, T., *J. Am. Chem. Soc.*, 77, 3651, (1955).

112. Stolbern, M.A., Tweil, R.C., Steinbern, G.M., and Wagner-Jaureon, T., *J. Am. Chem. Soc.*, 77, 765, (1955).

113. Samuel, D. and Silver, B., *J. Am. Chem. Soc.*, 85, 1197, (1963).

114. Schwindler, R. and Steinbern, G.M., *J. Am. Chem. Soc.*, 78, 3594, (1956).

115. Green, A.L. and Saville, B.L., *J. Chem. Soc.*, 3887, (1965).

116. Epstein, J., Bauer, V.E., Saxe, M., and Demek, M.M., *J. Am. Chem. Soc.*, 78, 4068, (1956).

117. Lordi, N.G. and Epstein, J., *J. Am. Chem. Soc.*, 80, 509, (1958).

118. Jandorf, B.J., *J. Am. Chem. Soc.*, 78, 3686, (1956).

119. Wagner-Jaureon, T., Hackley, B.E., Lies, T.A., Owens, D.D., and Proper, R., *J. Am. Chem. Soc.*, 77, 922, (1955).

120. Courtney, R.C., Gustavson, R.L., Westerback, S.J., Hyytiainen, H., Chabereck, S.C., and Martell, A.E., *J. Am. Chem. Soc.*, 79, 3030, (1957).

121. Gustavson, R.L., Chabereck, S., and Martell, A.E., *J. Am. Chem. Soc.*, 85, 598, (1963).

122. Dimroth, K., Witzel, H., Hulsen, W., and Mirbach, H., *Ann. Chem.*, 620, 94, (1959).

123. Hoffman, F.W. and Reeves, A.M., *J. Org. Chem.*, 26, 3040 (1961).
Zeffert, B.M., Coulter, P.B., and Tannenbaum, H., *J. Am. Chem. Soc.*, 82, 3843 (1960)

124. Baier, R.W. and Weller, S.W., IAEC Process Design and Development, 6, 380 (1967).

125. Epstein, J., Personal Communication.

126. Swain, C.G., and Scott, C.B., *J. Am. Chem. Soc.*, 75, 141, (1953).

127. Bauer, V.E., Demek, M.M., Corey, G.G., and Epstein, J., "Chlorination of VX in Dilute Aqueous Solution at 25°C," CWLR-2231, August, 1958.

128. Coe, Perry, and Brown, *J. Chem. Soc.*, 3604, (1957).

129. Green, M. and Hudson, R.F., *J. Chem. Soc.*, 1004, (1963).

130. J.I.G. Cadogan, *J. Chem. Soc.*, 3067, (1961).

APPENDIX B
SCREENING OF POTENTIAL CHEMICAL METHODS

HYDROLYSIS OF THE AGENTS

- Caustic Hydrolysis
- Acid Catalyzed Hydrolysis
- Liquid (hot) Water Hydrolysis
- Steam Hydrolysis
- Super Critical Water Hydrolysis

TABLE B-1. CAUSTIC HYDROLYSIS OF GB

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (9)	10	9	90	- Same as CAMDS operations - Complete destruction can be achieved in seconds, at high pH.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/200	
Conditions and practicality of reactions Temperature + Pressure, Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	7	70	- Mild except for PH>12 - NaOH corrosive
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	10	100	- Done on pilot scale at CAMDS
Can handle impure agents Known (10) Expected (5)	10	5	50	- Presence of impurities is not a major problem. However it is not fully clear in case of thickened GB as found in some munitions.
Products are non-toxic	5	2	10	- Major products are salts that may regenerate GB.
Availability of reagents in large quantities	8	10	80	- NaOH is available at moderate cost.
Ability to handle whole munitions Known (10) Likely (6)	10	1	10	- Cannot handle intact shells - Hydrolysis is normally designed to pump liquids and not solids. Variations to wash off the metal and decontaminating, it is possible.

TOTAL = 510>450

TABLE B-1. CAUSTIC HYDROLYSIS OF GB (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products are useless salts
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	5	50	- H cannot be treated at room temp. because of poor solubil Reaction of VX is aslo extrem slow at low temperatures.
Environmental Impact of waste products	10	0	0	- Salts are difficult to disposi of because they can regenate GB. About 5 lbs of salts are generated per lb of agent.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- Mild conditions, also tested at CAMDS.
Overall economics Capital - 5 Operation - 5	10	3	30	- Expensive. It uses large amou of NaOH. The salts has to als stored in a safe place. Maint ance is likely to be high alsc
Probability of success, state of development, and ability to meet project schedule	10	9	90	because NaOH is corrosive. - Tested at CAMDS.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Demonstrated at CAMDS, showed moderate availability.
Automation capabilities and need for human interaction	7	7	49	- Could be automated. Salt section requires human attenti

TABLE B-1. CAUSTIC HYDROLYSIS OF GB (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	8	64	- The equipment can be easily detoxified by circulating a caustic solution through it. It can then be drained and washed with water and dried and Mothballed in a nitrogen environment. Before restarting the nitrogen may be bubbled through a caustic solution or incinerated to guard against possible contamination However left over salts may be a problem.
Turndown capability	7	6	42	- Can be turned down to partial loads by controlling flow rates. Flow ra of NaOH has to be carefully control in order to control the pH.
Site utility requirements	6	7	42	- NaOH has to be brought to the site large quantities but utility requirments are small and site does not s to be a major problem in this respe
Transportability of process	3	0	0	- Because the process produces salts need storage transportating the pro especially the section that handles solids is very difficult.
		TOTAL =	517	
		GRAND TOTAL =	510 + 517 = 1027	

General Comments

Production of large amounts of salts makes this process unfavorable.

TABLE B-2. CAUSTIC HYDROLYSIS OF VX

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- After long time and further processing.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	8	8/160	- Requires 6-8 hrs at 20°C but reduces fast with temperature, down to about 1 min at 150°C.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	5	50	- Mild conditions but NaOH is corrosiv
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Extrapolated from low temp. data.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected
Products are non-toxic	5	8	40	- A mixture of non-toxic salts is produced. Some might have some toxic properties
Availability of reagents in large quantities	8	9	72	- Same as for caustic hydrolysis of GE
Ability to handle whole munitions Known (10) Likely (6)	10	1	10	- Same as for caustic hydrolysis of GE

TOTAL = 422/450

TABLE B-8. STEAM HYDROLYSIS OF AGENTS

Steam hydrolysis of the agents is similar to the hot water hydrolysis except that it will be carried out at higher temperatures. The reactions will be gas phase or gas-liquid. Thus, this method is more complex and more expensive than hot water hydrolysis and that is why it received lower total scores with each of the three agents. The products are expected to be the same in both cases. Decomposition and pyrolysis may result at high temperatures and this results in numerous products which will reduce the value of key products.

TABLE B-2. CAUSTIC HYDROLYSIS OF VX (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	8	64	- See Same for GB
Turndown capability	7	6	42	- See Same for GB
Site utility requirement	6	7	42	- See Same for GB
Transportability of process	3	0	0	- See Same for GB
		TOTAL = 524		
		GRAND TOTAL = 432 + 524 = 956		

TABLE B-3. CAUSTIC HYDROLYSIS OF H

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Complete destruction may be achieved at high temp. and pressure and with recycle.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	8	80/160	- A solvent is needed to solubilize th mustard to achieve a fast reaction.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	5	50	- High temp. and pressure are needed t achieve practical reaction rates.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Based on extrapolated data from room temp.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected with similar capability as CAMDS.
Products are non-toxic	5	8	40	- Products are NaCl and thiodiglycol (1 both non-toxic. TDG may contain trac of H (not sure).
Availability of reagents in large quantities	8	8	64	- Both H_2O and NaOH are available in la quantities. Solvents may be recycled and are also available.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- See Same for GB.

TOTAL = 444 ≃ 450

TABLE B-3. CAUSTIC HYDROLYSIS OF H (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	5	50	- Thiodiglycol is sold in large quantities for about 63¢/lb.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	5	50	- Caustic hydrolysis can be used with all three agents. But wit difficulty for GB and VX.
Environmental Impact of waste products	10	8	80	- NaCl must be disposed of. No problem concerning regeneration of H since thiodiglycol will be removed.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- See same for GB
Overall economics Capital - 5 Operation - 5	10	5	50	- Liquid phase RX's. Small comme cially available unit operation
Probability of success, state of development, and ability to meet project schedule	10	6	60	- Not labor nor energy intensive no expensive reagents or R&D ne - Simple design - No hazardous byproducts to comp cate design by introducing spec treatment and disposal methods.
	Performance of The Process			
Reliability, availability, maintainability	10	6	60	- Commercially proven equipment
Automation capabilities and need for human interaction	7	8	56	- TAP sensors - Override controls and auto shut-off - Automatic feed - Little man-power

TABLE B-3. CAUSTIC HYDROLYSIS OF H (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	6	46	- See Same for GB
Turndown capability	7	6	42	- See Same for GB
Site utility requirement	6	5	30	- See Same for GB
Transportability of process	3	4	12	- See Same for GB
		TOTAL = 843		
		GRAND TOTAL = 444 + 843 = 1072		

TABLE B-4. ACID CATALYZED HYDROLYSIS OF GB AND H

The method which involves adding acid as a catalyst is similar to the hot water hydrolysis of GB after steady state is reached. Hot water hydrolysis of GB produces HF which catalyzes the reaction.

The reason that the two processes received different total score (i.e. 1164 for acid catalyzed and 1303 for hot water hydrolysis) is that the acid catalyzed case was evaluated at room temperature while hot water hydrolysis was evaluated at 150°C. This resulted in more favorable kinetics for the hot water hydrolysis case.

The same thing applies in the case of H. Acid catalyzed hydrolysis involves addition of HCl while in the case of hot water hydrolysis HCl is produced. HCl might have to be added to start the reaction. The difference in the total scores is due to the same reason described above.

Hot water hydrolysis is evaluated later.

TABLE B-5. ACID CATALYZED HYDROLYSIS OF VX

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Main reaction produces toxic chemicals Extensive further processing is required to detoxify them.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	2	20/70	- Reaction rate is slow at room temperat
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	50	- Room temperature
Confidence in the reactions CODS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Extrapolated from limited lab data.
Can handle impure agents Known (10) Expected (5).	10	5	50	
Products are non-toxic	5	0	50	- This method produces toxic compounds which could not be disposed of without extensive further processing.
Availability of reagents in large quantities	8	9	80	- Water is available, moderate amount needed.
Ability to handle whole munitions Known (10) Likely (6)	10	4	0	- Cannot handle intact shells. - Hydrolysis is normally designated to pump liquids and not solids. Variations to wash off the metal and decontaminating it is possible.

TOTAL = 272<450

STOP Process rejected

TABLE B-6. HOT WATER HYDROLYSIS OF VX

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- VX is not very well miscible in water. Ethanolamine is added to solubilize it - Kinetic info extrapolated from 0-30°C it suggests that complete destruction can be achieved in seconds.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/190	
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	7	70	- 150°C - No corrosive products
Confidence in the reactions CWIOS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Extrapolated from lab data in the range 0-30°C.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Presence of impurities is not a major problem, however effect is not fully known.
Products are non-toxic	5	7	35	- Major products are water soluble salts that present no serious toxicity problems.
Availability of reagents in large quantities	0	10	80	- Water is available, moderate amounts needed.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot handle intact shells. - Hydrolysis is normally designated to pump liquids and not solids. Variations to wash off the metal and decontaminatinn it is possible.

TOTAL = 475>450

TABLE B-6. HOT WATER HYDROLYSIS OF VX (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products are useless water soluble salts.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Hydrolysis can be used with all three agents.
Environmental Impact of waste products	10	3	30	- The water soluble salts had to be incinerated.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- Special designs may be needed t accommodate 150°C and 100 psi though not severe.
Overall economics Capital - 5 Operation - 5	10	9	90	- Liquid phase RX's. Small commercially available unit operations.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Not labor nor energy intensive and no expensive reagents or R&I needed. - Chemistry is fairly known. - Simple design. - No hazardous byproducts to complicate design by introducing special treatment and disposal methods.
Performance of The Process				
Reliability, availability, maintainability	10	7	70	- Commercially proven equipment.
Automation capabilities and need for human interaction	7	8	56	- T&P sensors - Override controls and auto shut-off. - Automatic feed - Little man-power

TABLE B-6. HOT WATER HYDROLYSIS OF VX (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	9	72	- The equipment can be easily detoxified by circulating a decon solution through it. It can then be drained and washed with water and dried and mothballed in a nitrogen environment. Before restarting the nitrogen may be bubbled through a decon solution or incinerated to guard against possible contamination. Some salt may be trapped.
Turndown capability	7	10	70	- Can be turned down to partial loads by controlling flow rates. - Heating may be automatically adjusted
Site utility requirement	6	7	42	- Heating fuel and water may have to be transported to some of the sites.
Transportability of process	3	6	18	- Process is simple - made up of pumps, heaters, and one column. May be easil transportable by rail. This can be further facilitated be designing it in modular form.
		TOTAL =	678	
		GRAND TOTAL =	475 + 678 = 1153	

TABLE B-7. HOT WATER HYDROLYSIS OF H

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	7	70	- H is not soluble in water. Acetone or DMSO will be added to solubilize it.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/170	- Kinetic infor extrapolated.it sugges that complete destruction can be act in 1 second at 150°C.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	6	60	- 150°C - HCl is produced and is corrosive.
Confidence in the reactions CHEMS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Extrapolated from lab data at lower temperatures.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Presence of impurities is not a majo problem.
Products are non-toxic	5	8	40	- Major products HCl and thiodiglycol ; sent no serious toxicity problems.
Availability of reagents in large quantities	8	10	80	- Water is available, moderate amounts needed.
Ability to handle whole munitions Known (10) Likely (5)	10	0	0	- Cannot handle intact shells. - Hydrolysis is normally designated to pumn linuids and not solids. Variations to wash off the metal and contaminating it is possible.

TOTAL = 440-450

TABLE B-7. HOT WATER HYDROLYSIS OF H (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	5	50	- Thiodyglycol may be used to pro duce binary munition for H if interest in it exist. It can a be sold since it is used in in- dustry.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Hydrolysis can be used with all three agents
Environmental Impact of waste products	10	9	90	- All products can be used in in- dustry or the military. No sub stantial amounts for disposal.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- Special designs may be needed t accommodate 150°C and 100 psi though not severe.
Overall economics Capital - 5 Operation - 5	10	9	90	- Liquid phase RX's. Small comm cially available unit operatior
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Not labor nor energy intensive no expensive reagents or R&D ne - Chemistry is known. - Simple design. - No hazardous byproducts to comp cate design by introducing spec treatment and disposal methods
Performance of The Process				
Reliability, availability, maintainability	10	7	70	- Commercially proven equipment
Automation capabilities and need for human interaction	7	8	56	- T&P sensors - Override controls and auto shut off - Automatic feed - Little man-power

TABLE B-7. HOT WATER HYDROLYSIS OF H (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	10	- The equipment can be easily detoxified by circulating a decon solution through it. It can then be drained and washed with water and dried and Mothballed in a nitrogen environment. Before restarting the nitrogen may be bubbled through a decon solution or incinerated to guard against possible contamination.
Turndown capability	7	10	70	- Can be turned down to partial loads by controlling flow rates. - Heating may be automatically adjusted.
Site utility requirement	6	7	42	- Heating fuel and water may have to be transported to some of the sites.
Transportability of process	3	5	15	- Process is simple - made up of pumps, heaters, and columns may be easily transportable by rail. This can be further facilitated by designing it in modular form.
		TOTAL = 793		
		GRAND TOTAL = 440 + 793 = 1233		

TABLE B-8. STEAM HYDROLYSIS OF AGENTS

Steam hydrolysis of the agents is similar to the hot water hydrolysis except that it will be carried out at higher temperatures. The reactions will be gas phase or gas-liquid. Thus, this method is more complex and more expensive than hot water hydrolysis and that is why it received lower total scores with each of the three agents. The products are expected to be the same in both cases. Decomposition and pyrolysis may result at high temperatures and this results in numerous products which will reduce the value of key products.

TABLE B-9. SUPER CRITICAL WATER HYDROLYSIS

This method was evaluated and rejected. The primary reasons for its rejection were:

(1) It requires very high pressures and thus causes a safety problem. The high pressure operation also increases the cost significantly.

(2) It does not seem to have any advantages over hot water hydrolysis.

Comparison of the results obtained and the discussion presented for each of the hydrolysis processes suggest that hot water hydrolysis is the most promising method. The reasons being:

(1) Most economical and simplest to design and operate.

(2) Does not produce salts except in the case of VX. However these salts are unlikely to regenerate VX and are non-toxic.

PYROLYSIS

- Conventional Pyrolysis
- Pyrolysis Using Microwave Heating
- Pyrolysis Using RF Heating

TABLE 10. CONVENTIONAL PYROLYSIS OF GB

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Complete decomposition will occur at 560°C - Irreversible because propylene is produced and leaves the products
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/180	- Required residence time is on the order of seconds at high temperature.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- Very high temps. are required.
Confidence in the reactions C:HOS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Tested at lab scale
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected. Depends on nature and decomposition temperature of the impurities.
Products are non-toxic	5	8	40	- Products are propylene, DF, MPA and MFPA all non-toxic.
Availability of reagents in large quantities	8	10	80	- None required.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Possible with special design of the pyrolysis chamber.

TOTAL = 480>450

TABLE 10. CONVENTIONAL PYROLYSIS OF GB (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	10	100	- Pyrolysis is 1st step to produce DF from GB. Propylene ca also be used as fuel.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Pyrolysis of the three agents possible, however in the case of H products contain vesicant
Environmental Impact of waste products	10	8	80	- Very small amounts of wastes will require disposal.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- High temperature but moderate pressures.
Overall economics Capital - 5 Operation - 5	10	5	50	- Energy intensive
Probability of success, state of development, and ability to meet project schedule	10	7	70	- Pyrolysis of hydrocarbons is a well known process.
	Performance of The Process			
Reliability, availability, maintainability	10	7	10	- Simple design, few moving parts accumulation of solid by products could be a problem.
Automation capabilities and need for human interaction	7	7	49	- Can be automated. However because of high temperatures careful monitoring is necessary.

TABLE 10. CONVENTIONAL PYROLYSIS OF GB (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- The equipment can be easily detoxified by heating at high temperature f a period of time. Equipment can be put back up on stream in a short peri of time.
Turndown capability	7	10	70	- Can be turned down to partial loads by controlling flow rates. - Heating may be automatically adjusted.
Site utility requirement	6	5	42	- Heating fuel may have to be transporte to some of the sites since large amount of it may not be readily available.
Transportability of process	3	7	15	- Process is simple - made up of pumps, heaters, and column may be easily trans portable by rail.
		TOTAL = 740		
		GRAND TOTAL = 480 + 740 = 1220		

TABLE 11. CONVENTIONAL PYROLYSIS OF VX

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Complete decomposition will occur at T>435°C. - Irreversible because ethylene is produced and leaves the products.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/180	- Required residence time is on the order of seconds at high temperatures
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- Very high temps. are required.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Tested at lab scale.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected. Depends on nature and decomposition temperature of the impurities.
Products are non-toxic	5	8	40	- Products are relatively non-toxic water soluble salts.
Availability of reagents in large quantities	8	10	80	- None required.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Possible with special design of the pyrolysis chamber.

TOTAL = 480>450

TABLE 11. CONVENTIONAL PYROLYSIS OF VX (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- No useful products.
Flexibility of the process, equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Pyrolysis of the three agents possible, however in the case of H products contain vesicants
Environmental impact of waste products	10	4	40	- Produces sals that require disposal.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- High temperature but moderate pressure
Overall economics Capital - 5 Operation - 5	10	8	80	- Energy intensive but less equipment since no product separation is needed.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Pyrolysis of hydrocarbons is a well known process.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Simple design, few moving parts accumulation of solid by product could be a problem.
Automation capabilities and need for human interaction	7	7	49	- Can be automated. However because of high temperatures careful monitoring is necessary.

TABLE 11. CONVENTIONAL PYROLYSIS OF VX (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- See Same for GB
Turndown capability	7	10	70	- See Same for GB
Site utility requirement	6	5	30	- See Same for GB
Transportability of process	3	7	21	- See Same for GB
		TOTAL = 640		
		GRAND TOTAL = 480 + 640 = 1120		

TABLE 12. CONVENTIONAL PYROLYSIS OF H

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Complete decomposition will occur a T>450°C . - Irreversible because gas mixture produced and leaves the products.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	6	60/140	- Required residence time is on the or of seconds at high temperature
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- Very high temps. are required.
Confidence in the reactions CHAOS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	5	50	- Tested at lab scale.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected. Depends on nature and decomposition temperature of the impurities.
Products are non-toxic	5	0	0	- Products are expected to contain vesicants.
Availability of reagents in large quantities	8	10	80	- None required.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Possible with special design of the pyrolysis chamber

TOTAL = 310<450

TABLE 12. CONVENTIONAL PYROLYSIS OF H (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Useless gas mixture and a mixt of liquids containing vesicant
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Pyrolysis of the three anents possible, however in the case products contain vesicants.
Environmental Impact of waste products	10	0	0	- See above.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- High temperature but moderate pressure.
Overall economics Capital - 5 Operation - 5	10	6	60	- Energy intensive products also require treatment and disposal
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Pyrolysis of hydrocarbons is a well known process.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Simple design, few moving part accumulation of solid by prod could be a problem.
Automation capabilities and need for human interaction	7	7	49	- Can be automated. However because of high temperatures cari monitoring is necessary.

TABLE 12. CONVENTIONAL PYROLYSIS OF H (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- The equipment can be easily detoxifi by heating at high temperature for a period of time. Equipment can be pu back on stream in a short period of
Turndown capability	7	10	70	- Can be turned down to partial loads l controlling flow rates. - Heating may be automatically adjustec
Site utility requirement	6	5	30	- Heating fuel may have to be transport to some of the sites since large amou of it may not be readily available.
Transportability of process	3	7	21	- Process is simple - made up of pumps and heaters. May be easily transport by rail.
		TOTAL =	530	
		GRAND TOTAL =	390 + 580 = 970	

TABLE 13. PYROLYSIS OF GB USING MICROWAVE

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Same as in the case of conventional pyrolysis.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/180	- Same as in the case of conventional pyrolysis.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (9) (2) 150°C (5) 300°C (2)	10	1	10	- Same as in the case of conventional pyrolysis.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Same as in the case of conventional pyrolysis.
Can handle agent Known (10) Expected (5)	10	5	50	- Same as in the case of conventional pyrolysis.
Products are non-toxic	5	8	40	- Same as in the case of conventional pyrolysis.
Availability of reagents in large quantities	0	10	60	- Same as in the case of conventional pyrolysis.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Same as in the case of conventional pyrolysis.

TOTAL = 480>450

TABLE 13. PYROLYSIS OF GB USING MICROWAVE (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	10	100	- Same as in the case of conventio al pyrolysis.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Same as in the case of conventio al pyrolysis
Environmental Impact of waste products	10	8	80	- Same as in the case of conventio al pyrolysis.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- Same as in the case of conventio al pyrolysis.
Overall economics Capital - 5 Operation - 5	10	3	30	- Microwave system is more expen- sive and uses electricity which is more expensive than fossil fu
Probability of success, state of development, and ability to meet project schedule	10	7	70	- Same as in the case of conventio al pyrolysis.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Same as in the case of conventio al pyrolysis.
Automation capabilities and need for human interaction	7	8	56	- Same as in the case of conventio al pyrolysis.

TABLE 13. PYROLYSIS OF GB USING MICROWAVE (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Same as in the case of conventional pyrolysis.
Turndown capability	7	10	70	- Same as in the case of conventional pyrolysis.
Site utility requirement	6	5	30	- Requires large amounts of electricit
Transportability of process	3	7	21	- Same as in the case of conventional pyrolysis.
		TOTAL = 717		
		GRAND TOTAL = 480 + 717 = 1197		

TABLE 14. PYROLYSIS OF VX USING MICROWAVE

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Same as in the case of conventional pyrolysis.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/180	- Same as in the case of conventional pyrolysis.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- Same as in the case of conventional pyrolysis
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Same as in the case of conventional pyrolysis.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Same as in the case of conventional pyrolysis.
Products are non-toxic	5	8	40	- Same as in the case of conventional pyrolysis.
Availability of reagents in large quantities	8	10	80	- Same as in the case of conventional pyrolysis.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Same as in the case of conventional pyrolysis.

TOTAL = 480>450

TABLE 14. PYROLYSIS OF VX USING MICROWAVE (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Same as in the case of conventional pyrolysis.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Same as in the case of conventional pyrolysis.
Environmental Impact of waste products	10	4	40	- Same as in the case of conventional pyrolysis.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- Same as in the case of conventional pyrolysis.
Overall economics Capital - 5 Operation - 5	10	3	30	- Microwave system is expensive and uses electricity which is more expensive then fossil fuel.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Same as in the case of conventional pyrolysis.
Performance of The Process				
Reliability, availability, maintainability	10	7	70	- Same as in the case of conventional pyrolysis.
Automation capabilities and need for human interaction	7	8	56	- Easier to automate fossil fuel burners.

TABLE 14. PYROLYSIS OF VX USING MICROWAVE (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Same as in the case of conventional pyrolysis.
Turndown capability	7	10	70	- Same as in the case of conventional pyrolysis.
Site utility requirement	6	5	30	- Requires large amounts of electricity.
Transportability of process	3	7	21	- Same as in the case of conventional pyrolysis.
		TOTAL =	597	
		GRAND TOTAL =	480 + 597 = 1077	

TABLE 15. PYROLYSIS OF H USING MICROWAVES

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Same as in the case of conventional pyrolysis.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	6	60/140	- Same as in the case of conventional pyrolysis.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- Same as in the case of conventional pyrolysis.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	5	50	- Same as in the case of conventional pyrolysis.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Same as in the case of conventional pyrolysis.
Products are non-toxic	5	0	0	- Same as in the case of conventional pyrolysis.
Availability of reagents in large quantities	0	10	80	- Same as in the case of conventional pyrolysis.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Same as in the case of conventional pyrolysis.

TOTAL = 590<450

TABLE 15. PYROLYSIS OF H USING MICROWAVES (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Same as in the case of conven tional pyrolysis.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	7	70	- Same as in the case of conven tional pyrolysis.
Environmental impact of waste products	10	0	0	- Same as in the case of conven tional pyrolysis
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- Same as in the case of conven tional pyrolysis.
Overall economics Capital - 5 Operation - 5	10	3	30	- Microwave system is more expen sive than the conventional ca: It also used electricity whicl more expensive than fossil fu
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Same as in the case of conven- tional pyrolysis.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Same as in the case of conven- tional pyrolysis.
Automation capabilities and need for human interaction	7	8	56	- Easier to automate than fossil fuel furnaces.

TABLE 15. PYROLYSIS OF H USING MICROWAVE (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Same as in the case of conventional pyrolysis.
Turndown capability	7	10	70	- Same as in the case of conventional pyrolysis.
Site utility requirement	6	5	30	- Requires large amounts of electricity
Transportability of process	3	7	21	- Same as in the case of conventional pyrolysis.
		TOTAL =	557	
		GRAND TOTAL =	390 + 557 = 947	

TABLE B-16. PYROLYSIS OF GB USING RF HEATING.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- See Same for conventional pyrolysis of GB.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/200	- See Same for conventional pyrolysis of GB.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- See same for conventional pyrolysis of GB.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- See same for conventional pyrolysis of GB.
Can handle impure agents Known (10) Expected (5)	10	5	50	- See same for conventional pyrolysis of GB.
Products are non-toxic	5	10	50	- See same for conventional pyrolysis of GB.
Availability of reagents in large quantities	8	10	80	- Moderate amounts of electricity neede - Electricity available.
Ability to handle whole munitions Known (10) Likely (5)	10	6	60	- Same as for conventional pyrolysis of GB.

TOTAL = 510>450

TABLE B-16. PYROLYSIS OF GB USING RF HEATING (cont.).

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	5	50	- See same for conventional pyrolysis of GB.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- See same for conventional pyrolysis of GB.
Environmental Impact of waste products	10	7	70	- See same for conventional pyrolysis of GB.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- See same for conventional pyrolysis of GB.
Overall economics Capital - 5 Operation - 5	10	2	20	- High capital and operating
Probability of success, state of development, and ability to meet project schedule	10	4	40	- New technology may not be a to meet project schedule.
Reliability, availability, maintainability	10	5	50	- New equipment may require a of maintenance.
Automation capabilities and need for human interaction	7	5	35	- Should be easy. However, cl human monitoring might also l required.

TABLE B-16. PYROLYSIS OF GB USING RF HEATING (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- See same for pyrolysis using microwaves.
Turndown capability	7	10	70	- See same for pyrolysis using microwaves.
Site utility requirement	6	2	12	- See same for pyrolysis using microwaves.
Transportability of process	3	6	18	- See same for pyrolysis using microwaves.
		TOTAL =	595	
		GRAND TOTAL =	510 + 595 = 1105	

TABLE B-17. PYROLYSIS OF VX AND H USING RF HEATING.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- See same for conventional pyrolysis of VX and H.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/200	- See same for conventional pyrolysis of VX and H.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	1	10	- See same for conventional pyrolysis of VX and H.
Confidence in the reactions CHEDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- See same for conventional pyrolysis of VX and H.
Can handle impure agents Known (10) Expected (5)	10	5	50	- See same for conventional pyrolysis of VX and H.
Products are non-toxic	5	10	50	- See same for conventional pyrolysis of VX and H.
Availability of reagents in large quantities	8	10	80	- Need moderate amounts of electricity - Electricity available.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Can not penetrate shell.

TOTAL = 510-450

TABLE B-17. PYROLYSIS OF VX AND H USING RF HEATING (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- See same for conventional pyrolysis of VX and H.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- See same for convetional pyrolysis of VX and H.
Environmental Impact of waste products	10	3	30	- See same for conventional pyrolysis of VX and H.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- See same for conventional pyrolysis of VX and H.
Overall economics Capital - 5 Operation - 5	10	2	20	- High capital and operating cost
Probability of success, state of development, and ability to meet project schedule	10	4	40	- New technology may not meet project schedule.
Reliability, availability, maintainability	10	5		- New equipment may require a lot of maintenance.
Automation capabilities and need for human interaction	7	5		- See same for pyrolysis using microwaves.

TABLE B-17. PYROLYSIS OF VX AND H USING RF HEATING (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- See same for pyrolysis using microwaves.
Turndown capability	7	10	70	- See same for pyrolysis using microwaves.
Site utility requirement	6	2	12	- See same for pyrolysis using microwaves.
Transportability of process	3	6	18	- See same for pyrolysis using microwaves.
		TOTAL =	505	
		GRAND TOTAL =	510 + 505 = 1015	

Comparison of the results obtained ard the discussion presented for each of the pyrolysis methods suggest that conventional pyrolysis is the most promising of the three. The reasons being:

(1) Most economical and simplest to design and operate.
(2) More industrial experience with conventional pyrolysis in general than with RF and microwaves.. Thus it is likely to be more reliable.

REACTIONS WITH CHLORINE CONTAINING COMPOUNDS

- Reaction with Chlorine in Aqueous Medium.
- Reaction with PCl_3 and PCl_5
- Reaction with Hypochlorites in Alkaline Solution
- Reaction with Thionyl Chloride

TABLE B-19. REACTION OF GB WITH CHLORINE IN ACID MEDIUM.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Extension processing required.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	1	10/60 Reject	- Residence time of several hours expected.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	9	90	- Room temperature. Cl_2 is slightly corrosive.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- Not tested. No data.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Types of impurities could effect results
Products are non-toxic	5	5	25	- May contain small amounts of toxics.
Availability of reagents in large quantities	0	9	72	- Chlorine is available. Difficult to transport in large amounts.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- Cannot dissolve metal but can corrode it over long period.
		TOTAL =	367<450 Reject	

TABLE B-20. ACID CHLORINALYSIS OF VX IN AQUEOUS MEDIUM.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Can do so under right operating conditions.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	7	70	- It is expected to require several minutes at slightly different temp.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	9	90	- Room temperature - Cl_2 corrosive.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Tested on limited scale at CAMDS.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected. However effect of different types of impurities unknown.
Products are non-toxic	5	8	40	- Produces non toxic salts.
Availability of reagents in large quantities	8	9	72	- Cl_2 available. Difficult to transport in large quantities.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- Cannot dissolve metals but can corrode it over very long period.

TOTAL = 522>450

TABLE B-20. ACID CHLORINALYSIS OF VX IN AQUEOUS MEDIUM (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	4	40	- Produces salt that can be used to recover phosphorous.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	6	60	- Can handle VX and H but not good for GB
Environmental impact of waste products	10	2	20	- Produces salts
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	10	100	- No major problems anticipated.
Overall economics Capital - 5 Operation - 5	10	7	70	- Moderate capital and operating cost. Uses a lot of chlorine.
Probability of success, state of development, and ability to meet project schedule	10	9	90	- Tested successfully on small scale at CAMDS.
Reliability, availability, maintainability	10	8	80	- Few moving parts.
Automation capabilities and need for human interaction	7	5	35	- Need extensive sampling. Also produces salts that needs to be handled.

TABLE B-20. ACID CHLORINALYSIS OF VX IN AQUEOUS MEDIUM (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	9	72	- Simple to decontaminate and store primarily tanks and pumps.
Turndown capability	7	9	63	- Easy. Control flow rates.
Site utility requirement	6	8	48	- Does not require plenty of utilities.
Transportability of process	3	7	21	- Tanks - easy to transport.
		TOTAL =	699	
		GRAND TOTAL =	522 + 699 = 1221	

TABLE B-21. ACID CHLORINOLYSIS OF H IN AQUEOUS MEDIUM.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Reaction can proceed to completion in excess Cl_2 in water solution.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100	- Expected to be very rapid once the mustard is in solution. Thus a solvent is needed.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Near room temperature. Cl_2 is corrosive.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- No data available in literature.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected.
Products are non-toxic	5	2	10	- Intermediate steps produce vesicants.
Availability of reagents in large quantities	8	9	72	- Same as for chlorinolysis of VX.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- Same as for chlorinolysis of VX.

TOTAL = 482>450

TABLE B-21. ACID CHLORINOLYSIS OF H IN AQUEOUS MEDIUM (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products include a mixture of HCl and H SO - difficult to sell.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	6	60	- Can handle VX and H.
Environmental Impact of waste products	10	5	50	- Special case has to be excercise to insure that all vesicants intermediates are destroyed.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	9	90	- Safe - care must be exercised in handling intermediates.
Overall economics Capital - 5 Operation - 5	10	7	70	- Moderate capital and operating cost. Uses a lot of chlorine.
Probability of success, state of development, and ability to meet project schedule	10	5	50	- Not tested but confidence in chemistry is good.
Reliability, availability, maintainability	10	8	80	- Same as for chlorinolysis of VX.
Automation capabilities and need for human interaction	7	5	35	- Same as for chlorinolysis of VX.

TABLE B-21. ACID CHLORINOLYSIS OF H IN AQUEOUS MEDIUM (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	9	72	- Same as for chlorinolysis of VX.
Turndown capability	7	9	63	- Same as for chlorinolysis of VX.
Site utility requirement	6	9	48	- Same as for chlorinolysis of VX.
Transportability of process	3	7	21	- Same as for chlorinolysis of VX.
		TOTAL =	843	
		GRAND TOTAL =	460 + 843 = 1127	

TABLE B-22. REACTION OF GB WITH PHOSGENE.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Further processing needed for complete conversion.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	1	10/90	- Several hours may be needed.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	10	100	- Temp. between 20-30°C; no corrosive materials.
Confidence in the reactions CWIDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- Reaction is postulated in anology with reaction of diisopropylmethyl phosphona with phosgene.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected to handle impurities.
Products are non-toxic	5	8	40	- Main products include methyl phosphonochlorofluoride, isopropyl chloride, CO_2, DF.
Availability of reagents in large quantities	8	10	80	- Phosgene is widely used in industry.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Unlikely to handle whole munitions.

TOTAL = 390<450

TABLE B-22. REACTION OF GB WITH PHOSGENE.(cont.).

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	8	80	- Products may be used to produ binary munition compounds.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	4	40	- Applicable only to GB.
Environmental Impact of waste products	10	8	80	- All products can be used. No substantial amount for disposa
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	6	60	- Special designs may be needed accommodate phosgene.
Overall economics Capital - 5 Operation - 5	10	6	60	- Gas liquid RX's. Batch operat Special design for phosgene.
Probability of success, state of development, and ability to meet project schedule	10	5	50	- Chemistry is not very well kno - Simple design. - No hazardous by-products to co plicate design except because of phosgene.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Commercial equipment
Automation capabilities and need for human interaction	7	6	42	- T&P sensors - Override controls and auto shut off. - Automatic feed. - Little man-power.

TABLE B-22. REACTION OF GB WITH PHOSGENE (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- The equipment can be easily detoxified by circulating a decon solution through it. It can then be drained a washed with water and Mothballed in nitrogen environment. Before restart the nitrogen may be bubbled through a caustic solution or incinerated to quard against possible contamination.
Turndown capability	7	8	56	- Can be turned down to partial loads by controlling flow rates. - Temperature control should be handled carefully.
Site utility requirement	6	7	42	- Water will be required to scrub $COCl_2$ from CO_2 effluent.
Transportability of process	3	4	12	- Process is simple - made up of pumps, heaters, and column may be easily trar portable by rail. This can be further facilitated by designing it in modular form.
		TOTAL = 672		
		GRAND TOTAL = 390 + 672 = 1062		

TABLE B-23. REACTION OF GB WITH PCl_3 AND PCl_5.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	7	70	- Unknown.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	2	20/90 Reject	- Unknown, expected to be on the order of hours at room temperature.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Room temperature. Corrosive medium.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- Never tested.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	5	50	- Unknown, may include toxic compounds.
Availability of reagents in large quantities	8	7	56	- PCl_3 and PCl_5 are available.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- Unlikely

TOTAL = 386<450
Reject

TABLE B-24. ALKALINE HYPOCHLORINATION OF GB.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Will proceed to completion in excess (OCl^-).
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	7	70	- Expected to require a residence time of several minutes.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Room temperature, corrosive medium.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Never tested, good possibility for success.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected.
Products are non-toxic	5	4	20	- Produces salts which may contain toxic compounds. Regeneration of GB cannot also be ruled out.
Availability of reagents in large quantities	8	9	72	- Chlorine is available but difficult to transport in large quantities.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- Likely but not very promising.

TOTAL = 462>450

TABLE B-24. ALKALINE HYPOCHLORINATION OF GB (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	2	20	- Produces a mixture of H_2SOX and HCl that will have limited application.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Process equipment can handle a 3 agents but under different conditions.
Environmental impact of waste products	10	2	20	- Produces salt (NaCl)
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	10	100	- See same for chlorination of G
Overall economics Capital - 5 Operation - 5	10	6	60	- See same for chlorination of G
Probability of success, state of development, and ability to meet project schedule	10	8	80	- See same for chlorination of GI
Reliability, availability, maintainability	10	8	80	- See same for chlorination of GI
Automation capabilities and need for human interaction	7	5	35	- See same for chlorination of GI

TABLE B-24. ALKALINE HYPOCHLORINATION OF GB (cont.).

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Tanks and pumps. Simple to decon and stove specially that NaOH is present.
Turndown capability	7	9	63	- See same for GB chlorinolysis.
Site utility requirement	6	9	54	- See same for GB chlorinolysis.
Transportability of process	3	9	27	- See same for GB chlorinolysis.
		TOTAL =	719	
		GRAND TOTAL =	462 + 719 = 1181	

TABLE B-25. REACTION OF GB WITH THIONYL CHLORIDE.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Exten: of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Unknown. May do so in the presence of excess thionyl chloride.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/100 Reject	- Expected to require a residence time on the order of minutes.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Room temperature.
Confidence in the reactions CAIDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	5	50	- No experimental data.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected.
Products are non-toxic	5	5	25	- Produces SO_2 which needs scrubbing.
Availability of reagents in large quantities	0	7	56	- Thionyl chloride is available but expensive.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- Unlikely but possible over very long periods of time.

TOTAL = 401<450
Reject

TABLE B-26. ANHYDROUS CHLORINOLYSIS OF GB (AFTER PYROLYSIS OF GB).

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Chlorinolysis will be preceeded by pyrolysis which is expected to proce to completion in a matter of seconds Further processing (chlorination) is carried out to produce DF rather tha to destroy the agent. This should b kept in ming in evaluating this meth The first three criteria on this pag refer to pyrolysis or destruction of the agent, and this is discussed ear The following 4 criteria on this pag refer to the chlorinolysos process, they are self explanatory. The last one refers to pyrolysis. This type of evaluation could not be avoided be cause we are looking at a hybrid proc and that production of DF is the key feature of this method.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/200	
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	2	20	
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	
Can handle impure agents Known (10) Expected (5).	10	5	50	
Products are non-toxic	5	10	50	
Availability of reagents in large quantities.	8	10	80	
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	

TOTAL = 500>450

TABLE B-26. ANHYDROUS CHLORINOLYSIS OF GB (AFTER PRYOLYSIS OF GB) (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	8	80	- Produces DF. Could be of g value to the military.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Chlorination process can handle all 3 agents.
Environmental Impact of waste products	10	9	90	- CO_2 is the gaseous product environmental problem.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	10	100	- Room temperature and pressur
Overall economics Capital - 5 Operation - 5	10	5	50	- Low capital, uses large amou of chlorine.
Probability of success, state of development, and ability to meet project schedule	10	7	70	- Good chance based on chemist of similar compounds used in industry.
Reliability, availability, maintainability	10	10	100	- Few moving parts. Easy to cc trol. Part of process is bat Pyrolysis could be done inde- pendently.
Automation capabilities and need for human interaction	7	6	42	- Batch process needs human int action.

TABLE B-26. ANHYDROUS CHLORINOLYSIS OF GB (AFTER PYROLYSIS OF GB) (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	9	72	- Easy to decon and store - tanks and pumps when done independent of pyrolysis.
Turndown capability	7	10	70	- Easy. Control flow rates and batch quantities when done independent of pyrolysis.
Site utility requirement	6	8	48	- Needs small amounts of energy and water. Except for pyrolysis.
Transportability of process	3	3	15	- Pyrolysis process coupled with chlorinolysis is difficult to transport.
		TOTAL =	837	
		GRAND TOTAL =	500 + 837 = 1337	

TABLE B-27. ANHYDROUS CHLORINOLYSIS OF VX.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- See note 1 which follows.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	0	0/100	- See note 2 which follows.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- See note 3 which follows.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- See note 4 which follows.
Can handle impure agents Known (10) Expected (5)	10	5	50	- See note 5 which follows.
Products are non-toxic	5	10	50	- See note 6 which follows.
Availability of reagents in large quantities	8	10	80	- See note 7 which follows.
Ability to handle whole munitions Known (10) Likely (6)	10	4	40	- Unlikely. It takes very long time.

TOTAL = 440<450

TABLE B-27. ANHYDROUS CHLORINOLYSIS OF VX (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	6	60	- See note 8 which follows.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- See note 9 which follows.
Environmental Impact of waste products	10	10	100	- See note 10 which follows.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	10	100	- See note 11 which follows.
Overall economics Capital - 5 Operation - 5	10	6	60	- Capital cost low. Operating cost is high. Needs a lot of chlorine.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Never tested but based on chemistry of similar compounds looks promising.
Reliability, availability, maintainability	10	10	100	- Simple process. Few moving part Easy to control. Part of proces is batch.
Automation capabilities and need for human interaction	7	6	42	- Because part of process is batch it is difficult to fully automate.

TABLE B-27. ANHYDROUS CHLORINOLYSIS OF VX (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Tanks and pumps easy to decon and store.
Turndown capability	7	10	70	- Simple. Control flow rate and quantities in batch.
Site utility requirement	6	10	60	- Requires no water and only small amour of energy.
Transportability of process	3	5	15	- Tanks and pumps. Easy to transport.
		TOTAL = 865		
		GRAND TOTAL = 440 + 865 = 1305		

Note 1. The first step in the reaction sequence is chlorination. We already know that acid chlorinolysis works very well with VX in the aqueous medium. The chlorination step is the same reaction in non-aqueous medium. If anything, it should be faster because there is no solubility problem of VX as in the case of aqueous based chemistry. The chloroderivative (I) could be separated from the rest of the material by distillation and further processed by PCl_5 or thionyl chloride to get the dichloro-compound. This reaction may be expected to give >90% yield from compound (I) over a period of one or more hours, The dichloro could be converted to the difluoro by treatment with NaF in CCl_4. Fluorination with NaF does not require any special equipment. Distillation of difluoro may require special materials of construction. No problems are expected in the filtration and removal of NaCl from the reaction medium.

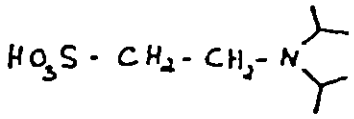
Note 2. The statements made in connection with H'agents apply in the case of VX. The reaction is expected to be vigorous, but at room temperature or below one would expect the conversion to take hours or more. Hence the score is zero.

Note 3. Same as in the case of H'agents. The reaction is expected to proceed at room temperature and atmospheric pressure. A maximum score of 8 is given for conditions and practicality. 2 points are taken off on the assumption that corrosion related problems may be encountered, though it is not expected to be a major factor.

Note 4. The confidence is based on the lab data from other conditions. In the case of VX, the acid chlorinolysis information should actually increase the score. However, this has not been done, to be on the safer side.

Note 5. Most of the impurities in CW agents are water insolubles. Aqueous based chemistries do not achieve the results expected of them from pure agents, because of the problem of mass transport. Therefore longer times, and less complete reactions than what is obtained with neat agents are encountered. Under non-aqueous conditions these difficulties are expected to be at best minimal, if not absent.

Note 6. The products are reactive, but non-toxic. After distilling off compound I, the sulfur compound could be hydrolyzed to non-toxic taurine deviative for instance.



Note 7. The same solvents and reagents as in the case of H'agents. Hence the same comments as in the case of mustard.

Note 8. The compound I could be converted to difluoro which is of some interest to the army. The route to difluoro can be accomplished under very mild conditions, using fairly inexpensive reagents. No special investments in the materials of construction for the reactor. The distillation assembly for difluror could be constructed of the same material as the storage vessels for difluoro.

Note 9. Refer the comments under H'agents.

Note 10. The products are reactive, but non-toxic. There is no danger of VX reformation. Once compound (I) is separated from the sulfur compound, the latter could be hydrolyzed and disposed off.

Note 11. The operations are all conducted at atmospheric pressure and room temperature. The solvents used are non-flammable.

TABLE B-28. ANHYDROUS CHLORINOLYSIS OF H.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	10	- See note 1 which follows.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	0	0/100	- See note 2 which follows.
Conditions and practicality of reactions Temperature + Pressure . Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- See note 3 which follows.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- See note 4 which follows.
Can handle impure agents Known (10) Expected (5).	10	5	50	- See note 5 which follows.
Products are non-toxic	5	10	50	- See note 6 which follows.
Availability of reagents in large quantities	8	10	80	- See note 7 which follows.
Ability to handle whole munitions Known (10) Likely (6)	10	6	60	- Likely but requires very long time.

TOTAL = 460>450

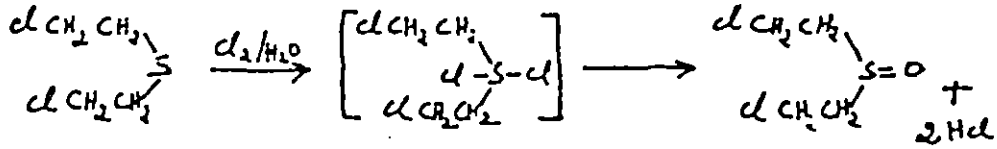
TABLE B-28. ANHYDROUS CHLORINOLYSIS OF H (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- See note 8 which follows.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- See note 9 which follows.
Environmental impact of waste products	10	10	100	- See note 10 which follows.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	10	100	- See note 11 which follows.
Overall economics Capital - 5 Operation - 5	10	5	50	- Capital cost is low. Operating cost is high. It needs a lot of chlorine.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Even though it was never tried before chemistry of similar compounds used in the pesticide industry is encouraging.
Reliability, availability, maintainability	10	10	100	- Simple process. Few moving parts (pumps.)
Automation capabilities and need for human interaction	7	6	42	- Part of the process will have to be done as batch. Difficult to fully automate.

TABLE B-28. ANHYDROUS CHLORINOLYSIS OF H (cont.)

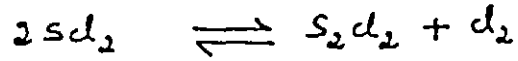
Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Tanks and pumps simple to decon and store.
Turndown capability	7	10	70	- Simple, control flow rates and quantities in batch.
Site utility requirement	6	10	60	- Require very little amounts of energy and no water.
Transportability of process	3	5	15	- Tanks and pumps, simple.
		TOTAL =	843	
		GRAND TOTAL =	460 + 843 = 1255	

Note 1. Extent of Reaction - H'agents are readily destroyed by all chlorinating agents both in aqueous and anhydrous medium. In the aqueous medium the reactions described in the equations at the beginning of this discussion would take a different course. These are as follows.

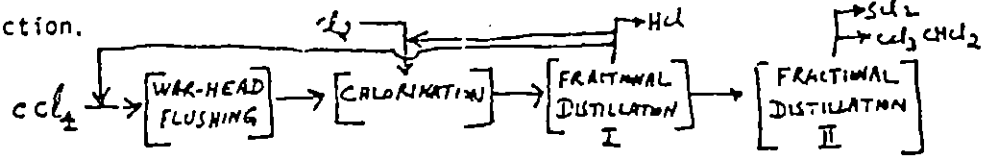


The sulfoxide is a vesicants, though not as effective as the H-agent. The toxicity is unacceptably high and the products would have to be chlorinated all the way to sulfate, chloride and carbon-dioxide to make sure toxic products are not present.

In the non-aqueous medium the compound I that is formed is rapidly isomerized to compound II and HCl. Compound II reacts further with chlorine followed by isomerization to give compound IV. Compound IV is non-toxic. Most likely, the chlorination cannot be stopped at this point. Therefore, one could assume that chlorination would proceed further until C-S clearage takes place. The end products of this reaction, in non-aqueous medium is therefore 1,1,1,2 tetrochloroethane, carbon-tetrochloride (solvent) and SCl_2. SCl_2 isomerizes readily as follows.



The boiling points of S_2Cl_2 (137°C), CCl_4 (767°C) and the tetrochloroethane (130.5°C) are sufficiently separated to allow fractional distillation and recovery of CCl_4 (B.P of H'agent 217°C). S_2Cl_2 is a powerful chlorinating agent in its own right. It reacts with metal hydroxides to give metal halides. It is used as a solvent for sulfur, as chlorinating agents and as intermediate S_2Cl_2 can be converted to SCl_2 by distilling from PCl_5. SCl_2 has a boiling point of 59°C, far removed from the boiling point of the tetrochloroethanes. The flow diagram such as the one given below can be suggested for further inspection.



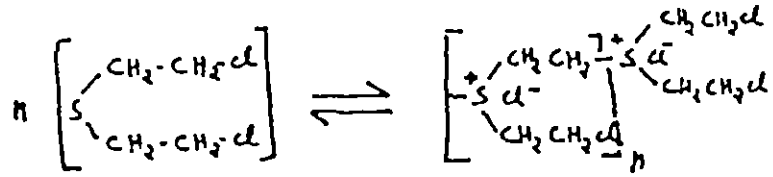
Note 2. The chlorination of sulfides are exothermic and the reaction is known to be fairly vigorous. However at room temperature or below one would reasonably expect conversion of all the H'agent to take hours rather than minutes. Hence the score is zero.

Note 3. The reaction should proceed at room temperature or below room temperature and at atmospheric pressure. A maximum score of 8 is given for conditions and practicality. 2 points are taken off for the corrosion related problems that may be encountered while handling sulfur halides, chlorine and HCl.

Note 4. The reactions are known to take place readily with all organic sulfides. Therefore scoring is based on data extrapolated from the laboratory conditions. Chlorination of mustard is known to be effective in aqueous conditions. However no data is seen on non-aqueous chlorination. In any case, the reactions may be expected to proceed as well or even better under nonaqueous conditions.

Note 5. One of the problems with H'agent when working with aqueous reagents is the very low solubility of the agent. This problem is eliminated with the use of CCl_4.

A second problem is the fact that most of the H'agent might have formed a gelatinous mass due to prolonged storage. It is well known that H-agents in concentrated solutions form sulfonium compounds such as those given below.



Compound V could form a polymeric gel which could undergo a variety of side reactions to give polysulfides and so on. During chlorination all these polysulfides are decomposed in the same manner as the H'agent and the portion that still remains in the form of V could depolymerise to the monomer, the H'agent, on dilution with CCl_4. Therefore nonaqueous chlorination should be particularly suited for handling polymeric sludges derived from H'agents

which are water insoluble. These sludges might be the major hurdle for any aqueous based chemistry.

Note 6. The end products of chlorination are unreacted chlorine, HCl and the halocarbons. None of them are toxic. The sulfur halides, S_2Cl_2 or SCl_2 is very reactive, but it is not toxic to the same extent as H'agent.

Note 7. The reagents that are used are CCl_4, Cl_2 and if necessary PCl_5. Both CCl_4 and Cl_2 are available in large quantities. The same is true of PCl_5. However PCl_5 is more expensive than the Cl_2 or CCl_4. If necessary one could eliminate the use of PCl_5 and think of other ways of removing S_2Cl_2.

Note 8. The halocarbons produced from H'agent can be used by industry as solvent. The sulfur halides are used as halogenating agents, solvents and so on. However, the major hurdle for industry to use it would be the suspicion that it might contain H'agent. Therefore the scoring is based on the assumption that neither industry nor military would use it. The score would be higher, if at a later stage it could be shown that the H'agent carried over or the toxicity data available could convincingly show the industry that these reagents, especially the sulfur halides, are perfectly safe for whatever use they are intended.

Note 9. The chlorination process can be adopted to all those agent. The same equipment and reagent could be used for VX and for GB.

Note 10. The halocarbons are produced in large quantities by petrochemical industry. Whatever means they use to dispose of it should be suitable, if it is decided to dispose of tetrachloroethane instead of finding a use for it as a solvent. The sulfur halides are rapidly hydrolysed to hydrochloric acid and sulfurous acid in aqueous solutions. These can be neutralized and disposed off as the salts or their solutions, if it is determined that the sulfur halides have no market.

Note 11. One of the problems of operating with organic solvents in non-aqueous phase is the danger of fire from flammable solvents. In the case of CCl_4, that danger is not present.

Examination of the screening of the different chlorination methods reveals that the following combination of methods are the best among the group.

(1) Anhydrous chlorinolysis of the three agents. In the case of GB the chlorinolysis process is preceeded by pyrolysis of GB.

(2) Aqueous chlorinolysis of VX and H and hypochlorination of GB under Alkaline conditions.

OXIDATION REACTIONS
(Excluding Incineration)

- Wet air oxidation
- Reactions with H_2O_2
- Reactions with O_3 in presence of UV

TABLE B-29. WET AIR OXIDATION OF GB.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	10	- This process is a combination of hot water hydrolysis of GB followed by oxidation.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/150	- Several minutes may be needed (based on results with simulants.)
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	0	0	- High temperatures and high pressures.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Tested with many different chemical wastes on large scale, but not with agents.
Can handle impure agents Known (10) Expected (5).	10	7	70	- Good chance it will.
Products are non-toxic	5	7	35	- Produces HF which should be handled with care.
Availability of reagents in large quantities	8	8	64	- Very large amounts of water are needed.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- Unlikely

TOTAL = 409<450

TABLE B-29. WET AIR OXIDATION OF GB (cont.).

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Oxidizes products to gases that need scrubbing and final dispos
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Can treat all three agents.
Environmental Impact of waste products	10	8	80	- Produces HF and P_2O_5 among othe Need scrubbing.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	- High temperatures and pressures
Overall economics Capital - 5 Operation - 5	10	5	50	- High temps and pressures result in high operating conditions. . All high pressure equipment is expensive.
Probability of success, state of development, and ability to meet project schedule	10	6	60	- This method is practiced in industry with different types of wastes but not with agents.
Reliability, availability, maintainability	10	6	60	- High pressure and temperature. Require moderate maintenance.
Automation capabilities and need for human interaction	7	7	49	- Easy to automate.

TABLE B-29. WET AIR OXIDATION OF GB (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	7		- Water had to be drained and system decontaminated. When re-starting system must be pressurized and re-heated.
Turndown capability	7	7		- Flow rate of agent may be controlled, without changing water flow rate or system temp. and pressure.
Site utility requirement	6	5		- Energy intensive. Requires a lot of electricity and heat.
Transportability of process	3	4		- Difficult to transport. Many componen
		TOTAL = 596		
		GRAND TOTAL = 409 + 596 = 1005		

TABLE B-30. WET AIR OXIDATION OF VX.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- See same for GB. The hydrolysis step will produce salts.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/140	- Several minutes may be needed.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	0	0	- See same for GB
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- The oxidation of the salts produced from the hydrolysis steo has not been tested.
Can handle impure agents Known (10) Expected (5).	10	7	70	- Good chance.
Products are non-toxic	5	7	35	- Produces some salts which may not be completely oxidized.
Availability of reagents in large quantities	8	8	64	- See same for GB.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- See same for GB.

TOTAL = 369<450

TABLE B-30.. WET AIR OXIDATION OF VX (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0		- See same for GB for the whole page except where reference to HF is made.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10		
Environmental Impact of waste products	10	8		
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5		
Overall economics Capital - 5 Operation - 5	10	5		
Probability of success, state of development, and ability to meet project schedule	10	6		
Reliability, availability, maintainability	10	6		
Automation capabilities and need for human interaction	7	7		

TABLE B-30. WET AIR OXIDATION OF VX (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8		7	- See same for GB for the whole nag
Turndown capability	7		7	
Site utility requirement	6		5	
Transportability of process	3		4	
		TOTAL = 396		
		GRAND TOTAL = 369 + 596 = 965		

TABLE B-31. WET AIR OXIDATION OF H.(cont.)

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- See same for GB. Products will include HCl, SO_2 which must be scrubbed.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	2	20/110	- It is expected to be long. Poor solubility of mustard is a major factor. A solvent might be needed.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	3	30	- See same for GB.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	2	20	- Never tested.
Can handle impure agents Known (10) Expected (5)	10	7	70	- Good chance
Products are non-toxic	5	7	35	- Scrubbing of SO_2, HCl must be done.
Availability of reagents in large quantities	8	8	64	- See same for GB
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- See same for GB

TOTAL = 369<450
Reject

TABLE B-32. OXIDATION OF GB USING H_2O_2

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Complete detoxification is possible though difficult. This is partly due to salt formation.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/150	- Required residence time is expected to be on the order of minutes.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (3) (2) 150°C (5) 300°C (2)	10	8	80	- Room temperature, corrosive conditions HF may be produced in the case of GB.
Confidence in the reactions CMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	6	60	- Tested on lab scale.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	9	45	- Produces salts and liquid wastes that are expected not to contain toxic compounds.
Availability of reagents in large quantities	8	7	56	- Both required reagents (H_2O_2 and NaOH are available in large quantities.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- Possible but not likely.

TOTAL = 471>450

TABLE B-32. OXIDATION OF GB USING H_2O_2 (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- None
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	6	60	- Can handle GB and VX.
Environmental Impact of waste products	10	0	0	- Produces salts.
Safety of operating conditions. 10 - intrinsic 5- with special engr.	10	8	80	- Safe. H_2O_2 should be handled with care.
Overall economics Capital - 5 Operation - 5	10	2	20	- H_2O_2 costly. Salt handling is also needed. Equipment moderat
Probability of success, state of development, and ability to meet project schedule.	10	7	70	- Not tested with agents but have good chance. H_2O_2 is a powerful reagent.
Reliability, availability, maintainability	10	7	70	- Simple process. Few moving parts. Corrosion moderate.
Automation capabilities and need for human interaction	7	8	56	- Possible. Salts require attention.

TABLE B-32. OXIDATION OF GB USING H_2O_2 (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	6	48	- Can be put in layaway. Fairly long time is needed to re-activate it.
Turndown capability	7	6	42	- Can be done. Flow rates will have to be controlled. Variable speed pumps may have to be used.
Site utility requirement	6	5	30	- Process requires water, electricity ar small amounts of fuel.
Transportability of process	3	4	12	- Not easy but can be built in Modular to facilitate that
		TOTAL = 488		
		GRAND TOTAL = 471 + 488 = 959		

TABLE B-33. OXIDATION OF VX USING H_2O_2

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	7	70	- Possible but difficult. This is partl due to salt formation.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/120	- Expected to be on the order of minutes
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- About room temperature.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	2	20	- Never tested.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected
Products are non-toxic	10	8	40	- Produces non-toxic salts that still require disposal.
Availability of reagents in large quantities	8	7	56	- Both H_2O_2 and NaOH are available.
Ability to handle whole munitions Known (10) Likely (6)	10	3	30	- Possible but not likely.

TOTAL = 396<450

Rejected

TABLE B-34. REACTION OF THE AGENTS WITH O_3 IN THE PRESENCE OF UV.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Results with other organic compounds indicate <2 ppb concentrations possible
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	0	0/100	- Rate limited by rate of UV. A 2-stage unit require 150 minutes to reduce DIMP from 3 PPM to <10 ppb.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	10	100	- Normal ambient conditions.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Has not been done with agents.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected.
Products are non-toxic	5	4	20	- Unless reactions is carried all the way toxic intermediates will be produced.
Availability of reagents in large quantities	0	8	64	- Requires electricity for UV and O_3 production. O_2 will also be required.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot handle metal shells.

TOTAL = 374<450

TABLE B-34. REACTION OF THE AGENTS WITH O_3 IN THE PRESENCE OF UV (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Unless process goes all the way to CO_2 toxic and useless compounds will result. No useful products when reaction goes all the way also.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100/100	- Can handle all 3 agents.
Environmental Impact of waste products	10	3	30	- If reaction is not carried all the way toxic products will result.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- O_3 is a health hazard. UV harmful to eyes. Easy to protect against both.
Overall economics Capital - 5 Operation - 5	10	7	70	- O_3 generators and UV lights hav low capacity, high cost. Operation and maintenance cost is also high.
Probability of success, state of development, and ability to meet project schedule	10	2	20	- Never tried. Proper operation requires product separation. Difficult.
Reliability, availability, maintainability	10	9	90	- UV lights require replacement. O_3 generators are rugged.
Automation capabilities and need for human interaction	7	8	56	- Considerable portion of the process is electrical, easy to automate.

TABLE B-34. REACTION OF THE AGENTS WITH O_3 IN THE PRESENCE OF UV.

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	9	72	- All parts can be easily stored.
Turndown capability	7	10	70	- Easy to run at reduced capacity by controlling O_3 rate.
Site utility requirement	6	5	30	- Requires large amounts of electricity which may not be available at some sit Availability of O_3 could also be a pro blem.
Transportability of process	3	6	18	- All units are modular or can be built as such.
		TOTAL =	636	
		GRAND TOTAL =	374 + 636 = 1010	

None of the oxidation methods described above seems promising for any of the agents. Oxidation also produces gaseous products that will need scrubbing, and does not produce any useful products.

OTHER METHODS

- Baking with soda ash
- Reactions with hydrogen and hydrides
- Reaction with decon solution (DS-a and CD-1)
- Reaction of H with sodium sulfite
- Reactions with sirbent and reactive resins
- Reaction of H with sodium metal
- Use of Na-PEG reagents
- Electrochemical methods
- Radiolysis using high energy electrons
- Direct interaction of microwaves with agents' molecules
- Photochemical reactions involving lasers
- Photolysis

TABLE B-35. BAKING OF GB WITH SODA ASH

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	2	20	- Equilibrium limited. Salt products can also reform GB.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	2	20/40	- Unknown, expected to be slow.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Near ambient.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	3	30	- No data available.
Can handle impure agents Known (10) Expected (5).	10	3	30	- Not expected.
Products are non-toxic	5	0	0	- Salt products can reform GB.
Availability of reagents in large quantities	8	10	80	- Soda ash can be derived from salts stored presently at CAMDS.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Unlikely.

TOTAL = 270<450

TABLE 3-36. REACTION OF AGENTS WITH HYDROGEN AND WITH HYDRIDES

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10			- Lack of information of these methods and the complexity of the reactions involved made it difficult to evaluate them meaningfully. Thus, they were rejected.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10			
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10			
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10			
Can handle impure agents Known (10) Expected (5)	10			
Products are non-toxic	5			
Availability of reagents in large quantities	8			
Ability to handle whole munitions Known (10) Likely (6)	10			

TABLE B-37. USE OF DECON SOLUTIONS (DS-2 AND CD-1) ON THE AGENTS.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- Similar to caustic hydrolysis but have low capacity - intended for decon rath than demil.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/140	- Could be made faster by increasing deco solution to agent ratio.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Near room temperature. Corrosiveness because of alkali presence.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	7	70	- Tested on large scale.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected.
Products are non-toxic	5	0	0	- Produce toxic compounds.
Availability of reagents in large quantities	8	10	80	- Army has large quantities.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot dissolve shells effectively.

TOTAL = 420/450

TABLE B-37. USE OF DECON SOLUTIONS (DS-2 AND CD-1) ON THE AGENTS (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Produce large volume of salts that require disposal.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Works on all three agents.
Environmental Impact of waste products	10	0	0	- Produces a large volume of di salt solution. This is a maj draw back of this method. Th salts may also regenerate the agents.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	5	50	
Overall economics Capital - 5 Operation - 5	10	7	70	- Requires large amounts of the decon solutions.
Probability of success, state of development, and ability to meet project schedule	10	7	70	- This method is more applicabl to decon cases then demil cas
Performance of The Process				
Reliability, availability, maintainability	10	10	100	- Simple batch process.
Automation capabilities and need for human interaction	7	8	56	- Automation possible

TABLE B-37. USE OF DECON SOLUTIONS (DS-2 AND CD-1) ON THE AGENTS.(cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Uses only tanks.
Turndown capability	7	10	70	- Simply by controlling amounts in batch.
Site utility requirement	6	10	60	- Little utility requirements.
Transportability of process	3	10	30	- Tanks can be decontaminated and transported easy.

TOTAL = 686

GRAND TOTAL = 420 + 686 = 1106

Eventhough this method has a moderate score it is rejected from further complications because it produces a large volume of waste containing numerous compounds many of which may be very toxic. Disposal of these wastes is a major problem. Thus the score that this method achieved may be misleading.

TABLE B-38. REACTION OF H WITH SODIUM SULFITE.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Mustard may be trapped in the polymer which results from the reaction.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50	- A solvent to solubilize H is required. Reaction to near completeness is still expected to take minutes.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	7	70	- Reactions occur near ambient temperature Slightly higher temps. are favored. Corrosive materials exist.
Confidence in the reactions CAIDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	8	80	- Thiokol tested this method on pilot scale.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected but never tested.
Products are non-toxic	5	5	25	- The products themselves are not toxic. However, H may be trapped within the polymer making it difficult to dispose of. The sulfites are available in large quantities from many vendors.
Availability of reagents in large quantities	0	10	80	
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot treat whole munitions - can not dissolve the metal nor treat the explosives.

TOTAL = 405<450

TABLE B-38. REACTION OF H WITH SODIUM SULFITE (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	3	30	- The rubber base polymer may be used except that it may contain untreated H.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	3	100	- Works only on H.
Environmental Impact of waste products	10		40	- Produces large volume of NaCl and sulfite salts. However could be disposed of.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- No safety problems envisioned b yond those associated with the agent. Simple batch process at near ambient conditions.
Overall economics Capital - 5 Operation - 5	10	8	80	- Uses commercially available and inexpensive equipment and reage Not energy nor labor intensive.
Probability of success, state of development, and ability to meet project schedule	10	3	80	- Tested on pilot scale.
	Performance of The Process			
Reliability, availability, maintainability	10	9	90	- Only tanks, batch process simple design few moving parts.
Automation capabilities and need for human interaction	7	6	42	- Difficult to automate because solids are produced. However simplicity of the process reduce the requirement for human interactions.

TABLE B-38. REACTION OF H WITH SODIUM SULFITE (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Batch process can be deconed and put in layaway.
Turndown capability	7	10	70	- Batch process easy to turn down by controlling amounts in batch.
Site utility requirement	6	9	54	- Requires only small amounts of energy and water.
Transportability of process	3	6	18	- Only tanks and pumps to transport. Simple
		TOTAL =	764	
		GRAND TOTAL =	405 + 764 = 1169	

TABLE B-39. USE OF REACTIVE AND SORBENT RESINS

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Similar concept to caustic hydrolysis When used with concentrated solution it will produce large amounts of salts which may regenerate some of the agent
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	10	100/50	- Rate is rapid.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	9	90	- Near ambient.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Tested only on very dilute water and air samples.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	0	0	- Produces salts which might trap or regenerate agent.
Availability of reagents in large quantities	8	6	48	- Reagents can be prepared in large quantities at moderate cost.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot handle metals and explosives

This low score coupled with the fact that large volumes of waste will be produced in the form of salts resulted in rejecting this method for this application.

TOTAL = 378/450

TABLE B-40. REACTION OF H WITH SODIUM METAL

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	5	50	- Not sure
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/100	- Expected to be on the order of minute:
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Near ambient
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	2	20	- Never tested - pure speculation.
Can handle impure agents Known (10) Expected (5)	10	2	30	- Not very likely.
Products are non-toxic	5	0	0	- Some by-products are toxic.
Availability of reagents in large quantities	8	5	40	- Sodium metal is available but expensiv and difficult to handle.(hazardous).
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot handle metals, explosives and other agents.

TOTAL = 270<450

TABLE B-41. USE OF Na-PEG FOR THE THREE AGENTS.

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	8	80	- Powerful reagents reactions should be complete. Possibility of trapping agent molecules in polymers exist.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	8	80/160	- Moderately fast. Some heating might be required to reduce the residence time to the one minute range.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	9	90	- Room temperature, however some heating might be needed to increase the rate. Little corrosion problems.
Confidence in the reactions CANDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Extrapolated from lab data on other compounds.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	8	40	- Non-toxic products are salts in the form of longer chains of PEG's.
Availability of reagents in large quantities	8	5	40	- Metallic sodium and polyethyleneglycol are available but not in much excess of requirements. Sodium is also hazardous to transport.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- No special capabilities for whole munitions.

TOTAL = 410<450

TABLE B-41. USE OF Na-PEG FOR THE THREE AGENTS (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products are salts, longer chains of PEG have no apparent value and require disposal.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Can be used for all 3 agents.
Environmental Impact of waste products	10	5 (GB) 7 (VX, HD)	50 70	- Salts will require proper disposal. Probably incineration first to reduce organic waste volume and then landfilling.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	7	70	- Large dilute volumes of waste will be produced.
Overall economics Capital - 5 Operation - 5	10	4	40	- Conditions are mild except tha metal is hazardous and difficu to handle. - Capital cost is low but cost o material is high, Na.
Probability of success, state of development, and ability to meet project schedule	10	8	80	- Although no work was done on tl with the agents the process is simple and should pose no majo difficulties.
	Performance of The Process			
Reliability, availability, maintainability	10	5	50	- Simple process however sodium related hazardscould cause emergency shutdowns.
Automation capabilities and need for human interaction	7	7	49	- Because of the nature of the products flow problems may complicate the automation of the process.

TABLE B-41. USE OF Na-PEG FOR THE THREE AGENTS (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Simple equipment (mixing tanks)
Turndown capability	7	10	70	- Easy to run at reduced scales.
Site utility	6	10	60	- Utility requirements are minimal.
Transportability of process	3	9	27	- Simple mixing tanks easy to transport.
		TOTAL =	678	
		GRAND TOTAL =	420 + 678 = 1098 for GB, 420 + 698 = 1118 for VX and H.	

The major drawback of this method is that it produces large volumes of dilute waste containing polymers that are difficult to dispose.

TABLE B-42. EVALUATION OF ELECTROCHEMICAL METHOD

Not enough information is available to apply the criteria to this method meaningfully. Literature on similar applications by Mann indicate that G agents are not electroactive while V agents are, and that it is extremely difficult to knock out the chlorine in the H agents electrochemically. In general, in an electrochemical cell one could accomplish an oxidation or a reduction. In GB and VX, the P-center is already fully oxidized. In VX the S & N could be oxidized to sulfonide, sulfone and the N-oxide. The sulfonide and sulfone are all toxic. The oxidized products from H are also toxic.

As far as reduction goes, very little information is available to predict if it will go all the way to phosphines. If it goes, there is not enough information on the rate and extent of conversion. The cell design will have to be complicated and the processing will become complex, both to operate and maintain. Therefore it is safe to say that electrochemical methods are not likely to be the leading candidates. More research has to be done in this area in future, before it can be even evaluated.

TABLE B-43. RADIOLYSIS OF GB, VX AND H USING HIGH ENERGY ELECTRONS (cont.)

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Very low concentrations can be achiev using large number of reactors.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/150	- Depends on dose rate - however rate i low per unit of radiation.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	10	100	- Room temperature and pressure and no corrosion.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	4	40	- Never tested. However radiation in general can destroy any organic molecule.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	5	25	- Products unknown.
Availability of reagents in large quantities	8	10	80	- Electricity is needed.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot penetrate metallic shells.

TOTAL = 445<450

TABLE B-43. RADIOLYSIS OF GB, VX AND H USING HIGH ENERGY ELECTRONS (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products unknown. Unlikely to be useful.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Can handle all 3 agents.
Environmental Impact of waste products	10	5	50	- Products unknown.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- Mild conditions - but electro beams are dangerous.
Overall economics Capital - 5 Operation - 5	10	4	40	- Capital cost for a 1000 lb/hr plant is about 13 million dollars, and electricity cost is about $1.1/lb.
Probability of success, state of development, and ability to meet project schedule	10	5	50	- Design of reactors has not bee done and process never tested with agents.
Reliability, availability, maintainability	10	5	50	- Equipment is complex.
Automation capabilities and need for human interaction	7	8	56	- Believed reasonable to do through equipment is complex.

SUB TOTAL = 426<450

TABLE B-43. RADIOLYSIS OF GB, VX AND H USING THE HIGH ENERGY ELECTRONS (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Equipment can be easily stored.
Turndown capability	7	10	70	- No problem
Site utility requirement	6	4	24	- Requires more than 1MW of electric source.
Transportability of process	3	5	15	- Equipment heavy but not large.
		TOTAL = 650		
		GRAND TOTAL = 426 + 650 = 1076		

TABLE B-44. DIRECT INTERACTION BETWEEN MICROWAVES AND MOLECULES OF G3, VX AND H

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	9	90	- Complete reaction is possible.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	5	50/140	- Reaction time on the order of 10 minutes expected.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	10	100	- Room conditions.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	2	20	- No data available.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected
Products are non-toxic	5	5	25	- A mixture will be produced some of which might be toxic.
Availability of reagents in large quantities	8	3	24	- Requires very large amounts of electricity at levels of gigahertz may be needed
Ability to handle whole munitions Known (10) Likely (6)	10	3		- Microwaves cannot penetrate metal shells. However, special jigs could perhaps be devised to insert the waves into the munit

TOTAL = 389/469

TABLW B-44. DIRECT INTERACTION BETWEEN MICROWAVES AND MOLECULES OF GB, VX AND H (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0		- No useful product.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Can be used with all three agents.
Environmental Impact of waste products	10	5	50	- Products unknown.
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- Special desions may be needed to shield process.
Overall economics Capital - 5 Operation - 5	10	3	30	- Microwave generators are expensive and uses electricity.
Probability of success, state of development, and ability to meet project schedule	10	3	30	- Unknown
Performance of The Process				
Reliability, availability, maintainability	10	6	60	- Microwave generators are conveniently available and tesed but not for this application.
Automation capabilities and need for human interaction	7	9	63	- T&P sensors. - Override controls and auto shut off - Automatic feed. - Little man-power.

TABLE B-44. DIRECT INTERACTION BETWEEN MICROWAVES AND MOLECULES OF GB, VX AND H (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	6	48	- Impact on microwave generators may be negative-long term contamination.
Turndown capability	7	10	70	- Can be turned down to partial loads by controlling microwave intensity.
Site utility requirement	6	5	30	- Large amounts of electricity needed.
Transportability of process	3	6	18	- Process is simple. Microwave generator sensitive
		TOTAL = 609		
		GRAND TOTAL = 389 + 609 = 998		

TABLE B-45. PHOTOCHEMICAL REACTIONS OF GB, VX AND H USING LASERS

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Can reach high destruction given the time and right conditions.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	0	0/100	- Takes long time
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	8	80	- Mild conditions. Laser beams may alter that slightly.
Confidence in the reactions CWDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	8	80	- Not tried before on agents. Tried on similar compounds only on bench scale.
Can handle impure agents Known (10) Expected (5)	10	5	50	- Expected
Products are non-toxic	5	5	25	- Products unknown.
Availability of reagents in large quantities	8	5	40	- Requires large amounts of electricity.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot penetrate the shell.

TOTAL = 335<450
Rejected

TABLE B-46. PHOTOLYSIS OF THE THREE AGENTS

Basic Chemistry Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Extent of reaction can it achieve the specified effluent concentration above (10) or with added processing (8)	10	10	100	- Can reach any desired extent given the time and conditions.
Rate of Reaction 10 sec (10) 1 min (8) 10 min (5) 1 hr (2)	10	0	0/100	- 20 hrs. This is based on reported results with dioxin.
Conditions and practicality of reactions Temperature + Pressure Corrosion Room (8) (2) 150°C (5) 300°C (2)	10	9	100	- Ambient conditions or slightly higher.
Confidence in the reactions CAMDS (10) Proved on pilot scale at demil conditions (8) Proved on lab scale at demil conditions (6) Extrapolated from lab data at other conditions (4)	10	9	90	- Tested with other organochlorine compounds on large scale.
Can handle impure agents Known (10) Expected (5).	10	5	50	- Expected
Products are non-toxic	5	5	25	- Unknown
Availability of reagents in large quantities	0	5	40	- Photolytic methods such as UV requires electricity. Large UV lamps will be needed.
Ability to handle whole munitions Known (10) Likely (6)	10	0	0	- Cannot penetrate the shell.

TOTAL = 405<450

TABLE B-46. PHOTOLYSIS OF THE THREE AGENTS (cont.)

Basic Process and Implementation Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Probability that military or industry will use products	10	0	0	- Products unknown.
Flexibility of the process equipment to handle all agents 3 Agents (10) 2 Agents (6) 1 Agent (3)	10	10	100	- Can handle all 3 agents.
Environmental Impact of waste products	10	5	50	- Products unknown
Safety of operating conditions 10 - intrinsic 5- with special engr.	10	8	80	- UV hazardous to eyes but easy to control.
Overall economics Capital - 5 Operation - 5	10	6	60	- Very large equipment - cost o equipment to handle 160 gallo batch is about $10,000. Need 31 such units to handle 1000 hr agent.
Probability of success, state of development, and ability to meet project schedule	10	5	50	- Process was not tried on agen and scale up of these has not been done.
	Performance of The Process			
Reliability, availability, maintainability	10	7	70	- Tubes have to be replaced. Fouling is a problem.
Automation capabilities and need for human interaction	7	9	63	- Can be easily automated. No significant problems.

TABLE B-46. PHOTOLYSIS OF THE THREE AGENTS (cont.)

Performance of the Process Criteria	Weight of Criterion	Criteria Score	Total Weighted Score	Remarks/Explanation
Layaway capability	8	10	80	- Equipment can be easily deconed and stored. Tanks and light sources.
Turndown capability	7	10	70	- Easy control batch and light source.
Site utility requirement	6	7	42	- Process requires less than 1 MW. No major problems.
Transportability of process	3	8	24	- Equipment not very large and not hea Easy to disassemble and assemble.
		TOTAL = 689		
		GRAND TOTAL = 405 + 689 = 1094		

HYBRID METHODS

Controlled Pyrolysis Followed by Reaction With

- PCl_5
- $SOCl_2$

TABLE B-47. HYBRID METHODS

A hybrid method for GB (Pyrolysis followed by chlorination) was described earlier. That method uses $COCl_2$. The methods mentioned here which used PCl_5 and $SOCl_2$follows the same pattern except that the when PCl_5 is used it will produce P_2O_5 as a by-product. Similarily using $SOCl_2$ will produce SO_2. Both gases require scrubbing while CO_2 does not. That is why these methods received lower score that pyrolysis followed by anhydrous chlorination of GB.

APPENDIX C

Linear flowrate of agent mixture in settling chamber:

$$V_l = \frac{Q}{\pi r^2}$$

where

V_l is linear velocity in cm/min
Q is volumetric flowrate in cm^3/min
r is radius of the settling chamber in cm.

Terminal velocity of particles under gravity:

$$V_p = \frac{40(\varsigma_p - \varsigma_f)\, g\, r_p^2}{3\, n}$$

where

V_p is the terminal velocity of particles in cm/min
ς_p is density of particles in g/cm^3
ς_f is density of fluid in g/cm^3
g is acceleration due to gravity, cm/sec
r_p is radius of the particle in cm
n is viscosity of the agent mixture, cp

Particle cut-off size r_c can be calculated by equating the right hand size of the two above equations. The result:

$$r_c = \frac{3\, n Q}{40\, \pi g\, (\varsigma_p - \varsigma_f)\, r^2}$$

The above equations are strictly valid for conditions in the Stoke's law region where the Reynolds number for settling of particles is less than 0.3. Calculated values of Reynolds number for settling of the smallest particles that can be separated with a given pipe size was of the order of 10. The error in calculation of the smallest particle size that can be removed by the 12-in. pipe due to the higher Reynolds number is about 10 percent. These calculations can be refined after more accurate data on flow rates and

viscosity become available. Impact of the minor changes on cost of the separation equipment is expected to be minimal.

For calculation purposes, ς_p was assumed to be equal to 3 g/cm^3; ς_f was assumed to be equal to 1 g/cm^3. Assumed values of n for various dilutions are shown below.

n, cp	Ratio of agent VX to diluent
12	1:0
6	1:1
4	1:3
3	1:5

APPENDIX D

1. INTRODUCTION

A reliability analysis has been completed for the Acid Hydrolysis Process for neutralization of chemical agents. The preliminary analysis has been based on the process for GB, because the process for GB is most complex, involving the most corrosive product (HF) and is, therefore, expected to be a "worst case" from a reliability standpoint. The following tasks have been accomplished in this effort:

- A failure modes and effects analysis was completed to better identify the interrelationships between the various system components and the types of failures that can occur.
- A fault tree logic diagram was developed to clarify the logical interrelationships between the various failure modes.
- "Down times" were estimated for each failure scenario (maintainabilities).
- A first estimate of system availability has been computed based on steps 1-3, above. The refined availability estimate was found to be 0.981.

2. GENERAL GROUND RULES FOR FIRST ORDER ESTIMATE

The basic assumptions and ground rules used for the reliability analysis are as follows:

1. It was assumed that system hardware failure is a reflection of part failure, i.e., system reliability is dependent upon each part of the system.
2. The exponential failure distribution was assumed valid.
3. The analysis was based on generic part failure rates and part count prediction techniques.
4. The operational failure rates were derived in accordance with the Parts Count Reliability Prediction method as given by the Nonelectric Parts Reliability Data Handbook, Rome Air Development Center, Griffiss AFB N.Y. based on a "Fixed Ground" environment, and a "Military Grade" quality factor. Some deviations to this procedure were necessitated because either the component is not included in the Handbook or no specific parts list now exists. In these cases data were obtained from the IEEE Std. 500-1977 "IEEE Guide to the Collection and Presentation of Electrical, Electronic, and Sensing Component Reliability Data for Nuclear-Power Generating Stations."
5. The part failure rates were assumed to be constant. This assumption was made in most cases due to the lack of data to the contrary.
6. It was assumed that the pumps, valves, controls, and other mechanical parts will be maintained and periodically checked for performance and replaced, as necessary, before wearout becomes a dominant failure consideration. Replacement parts were assumed to be on hand at the facility.
7. A duty cycle period of 120 hours continuous operations (5 days) and 48 hours (2 days) off time was considered during this reliability analysis. This assumes that the functional integrity of the process system is assured with an effective program of regularly scheduled preventative maintenance during the off time period of 48 hours. The preventative maintenance program would be comprised of several tasks including:
   (a) inspection, preventive replacement, or overhaul of short-life components particularly sensitive to wear such as the slip ring brush assembly, motor, valves, sensors, relays and other mechanical components

(b) calibration and alignment of electronic/regulator controls, limit switches, sensors, etc.

(c) lubrication and various house-cleaning tasks.

3. SPECIFIC ASSUMPTIONS MADE FOR RELIABILITY QUANTIFICATION

The following operational assumptions were made so that the system was sufficiently well defined to enable quantification.

1. Any detectable leak in the system will result in system shut down.
2. Only continuous operation has been considered, i.e., initial start-ups are not included in the analysis. This means that the system has been thoroughly "debugged" and the usual start-up problems have been eliminated.
3. Utilities (electricity, air, water, gas) are assumed to be available and their unavailability is not part of this analysis.
4. Sensor and control systems have not yet been defined for the acid hydrolysis system. For the purposes of the analysis, the following sensors are assumed to be present:
   (a) room air sensor for agent, HF, and MPA
   (b) agent/HF sensor on furnace and reboiler flue gases
   (c) pressure differential sensor on pumps
   (d) rpm indicator on pump and air cooler motors
   (e) temperature sensor on furnace and reboiler flue gases
   (f) closed circuit TV cameras for general observation
   (g) periodic sampling of process products, with an assumed forty-eight hour turnaround time of collection and analysis.

   As these systems are not as yet well defined, sensor failures were not included in the analysis. In particular, false alarms resulting in system shut down were not considered.
5. In order to maximize resistance to corrosion failure, it has been assumed that all piping connections are welded with the exception of those connecting the pumps, which are assumed to be flanged with o-rings. The pumps are expected to require periodic maintenance which will require them to be disconnected from the system, rendering welding inappropriate.
6. Any filter or settling tank which may be added to the system at its front end to remove impurities and/or solid particulates has not been included in this analysis.

7. Any scrubbers which may be attached to furnace or reboiler flue gases, to the room air exhaust, or to the storage tanks have not been considered.

8. It is assumed that enough replacement and repair areas are available so that any required repair work may be accomplished on a continuous basis; that is, repair work will not stop due to a lack of available personnel.

9. A product of the acid hydrolysis process is hydrofluoric acid, an extremely corrosive acid. Although a special alloy, Hastalloy B, is to be used in the system, it is likely that corrosion in the system will be more rapid than is normal in process systems, resulting in higher failure rates for system components. Therefore, the part failure rates in the reliability literature have been multiplied by an environmental factor to account for this effect. Based on corrosion data from the Chemical Engineer's Handbook, an environmental factor of 10 was estimated for those components which are in contact with HF. Those components in contact with MPA are assigned an environmental factor of five. All other components in contact with solutions that are possibly contaminated with HF and MPA were given a factor of three. It is felt that these estimates result in a conservative estimate of system reliability. Nevertheless, Figure D-1, at the end of this appendix, shows estimated system availability as a function of both less and more severe values of the corrosion factor α.

10. The estimated downtime (Table D-1) for any failure scenario was broken down into the following categories:

    (a) Sensing time--the time between system failure and the realization of that failure by system operators

    (b) Suitup time--the time required to shut down the system, while concurrently repair workers are putting on protective suits and are being checked out to enter the contaminated area. This time was estimated at 0.5 hr

    (c) Isolation time--the time required for repair workers to isolate the problem, e.g., find a leak in the system should the room air sensor detect the presence of agent

    (d) Repair time--time required to repair the failure

    (e) Startup--the time required to "warm-up" the system to the equilibrium state required in the columns after repair work has been completed. This time was estimated at 4 hr.

    The isolation and repair times were highly dependent on the particular failure involved. For example, if a small leak develops and GB is released, tripping the room air sensor, an extended period of time may be required to find the leak. A pump breakdown, on the other hand, may be sensed

TABLE D-1. DETAILS OF THE CALCULATION OF THE AVAILABILITY OF THE HYDROLYSIS PROCESS (page 1 of 3)

Comp. No.	Component	Failure Mode	Down Time* t_1	t_2	t_3	t_4	t_5	$\sum_{i=1}^{5} T_i$	λ (Failure Rate) Under Normal Conditions	Envir. Factor	Adjusted Failure Rate	u (Component Unavailability)
D-101	Feed Drum	Leak (major)	0	0.5	.25	1	4	5.75	1×10^{-9}	3	3×10^{-9}	1.73×10^{-8}
P-101	Main Pump	Leak	0	0.5	24	1	4	28.75	5.62×10^{-6}	3	1.69×10^{-5}	4.85×10^{-4}
		Both Pumps Unavailable						29	2.37×10^{-9}	3	7.11×10^{-9}	2.06×10^{-7}
⟨1⟩	Agent Feed Line	Leak	0	0.5	24	R	4	36.5	1×10^{-9}	3	3×10^{-9}	1.1×10^{-7}
F-101	Furnace	Leak (in Coil (in coil + 2 welds)	0	0.5	1	12	4	17.5	7×10^{-9}	10	7×10^{-8}	1.23×10^{-6}
		Burner Failure	0	0.5	0.5	R	4	13.0	4.6×10^{-5}	1	4.6×10^{-5}	5.98×10^{-4}
E-101	Static Mixer	Leak	0	0.5	24	R	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
DC 101	Bubble Cap Column	Leak	0	0.5	24	R	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
P-105	Pump	Leak	0	0.5	24	4	4	32.5	5.62×10^{-6}	5	2.81×10^{-5}	9.13×10^{-4}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	4.98×10^{-6}	5	2.49×10^{-5}	2.24×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	1	2.56×10^{-6}	2.2×10^{-5}
F-102	Reboiler	Leak in Coil	0	0.5	1	12	4	17.5	7×10^{-9}	5	3.5×10^{-8}	6.13×10^{-7}
		Burner Fails	0	0.5	0.5	R	4	13.0	4.6×10^{-5}	1	4.6×10^{-5}	5.98×10^{-4}
C-101	Air Cooler	Coil Leaks	0	0.5	24	R	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
		Blower Fails	0	0.5	0.5	4	4	9	3.809×10^{-6}	1	3.809×10^{-6}	3.43×10^{-5}
D-102	Reflux Drum	Leak	0	0.5	24	R	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
P-107	Reflux Pump	Leak	0	0.5	24	4	4	32.5	1.01×10^{-5}	10	1.01×10^{-4}	3.28×10^{-3}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	8.98×10^{-6}	10	8.94×10^{-5}	8.05×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	1	2.56×10^{-6}	2.30×10^{-5}
BV-102	Block Valve	Leak	0	0.5	48	R	4	60.5	6.47×10^{-7}	10	6.47×10^{-6}	3.91×10^{-5}
BV-103	Block Valve	Leak	0	0.5	48	R	4	60.5	6.47×10^{-7}	10	6.47×10^{-6}	3.91×10^{-5}
BV-101	Block Valve	Leak	0	0.5	24	R	4	36.5	6.47×10^{-7}	10	6.47×10^{-6}	2.36×10^{-4}
DC-102	Packed Column	Leak	0	0.5	24	R	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}

TABLE D-1. DETAILS OF THE CALCULATION OF THE AVAILABILITY OF THE HYDROLYSIS PROCESS (page 2 of 3)

Comp. No.	Component	Failure Mode	Down Time* t_1	t_2	t_3	t_4	t_5	$\sum_{i=1}^{5} T_i$	λ (Failure Rate) Under Normal Conditions	Envir. Factor	Adjusted Failure Rate	u (Component Unavailability)
P-106	Pump	Leak	0	0.5	24	4	4	32.5	1.01×10^{-5}	10	1.01×10^{-4}	3.28×10^{-3}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	8.94×10^{-6}	10	8.94×10^{-5}	8.05×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	1	2.56×10^{-6}	2.30×10^{-5}
F-103	Reboiler	Leak in Coil	0	0.5	1	12	4	17.5	7×10^{-9}	10	7×10^{-8}	1.23×10^{-6}
		Burner Fails	0	0.5	0.5	8	4	13.0	4.6×10^{-5}	1	4.6×10^{-5}	5.98×10^{-4}
C-103	Air Cooler	Coil Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3×10^{-9}	1.10×10^{-7}
		Blower Failure	0	0.5	0.5	4	4	9.0	3.809×10^{-6}	1	3.809×10^{-6}	3.43×10^{-5}
D-103	Reflux Drum	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3×10^{-9}	1.10×10^{-7}
P-103	Reflux Pump	Leak	0	0.5	24	4	4	32.5	1.01×10^{-5}	3	3.03×10^{-5}	9.85×10^{-4}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	8.49×10^{-6}	3	2.55×10^{-5}	2.29×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	3	7.68×10^{-6}	6.91×10^{-5}
C-104	Air Cooler	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3×10^{-9}	1.10×10^{-7}
		Blower Fails	0	0.5	0.5	4	4	9.0	3.809×10^{-6}	3	1.14×10^{-5}	1.03×10^{-4}
T-101	Tank	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3×10^{-9}	1.10×10^{-7}
C-105	Air Cooler	Coil Leak	0	0.5	24	8	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
		Blower Fails	0	0.5	0.5	4	4	9.0	3.809×10^{-6}	1	3.809×10^{-6}	3.43×10^{-5}
T-102	Tank	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	10	1×10^{-8}	3.65×10^{-7}
BY-104	Block Valve	Leak	0	0.5	24	8	4	36.5	6.47×10^{-7}	5	3.24×10^{-6}	1.18×10^{-4}
BY-105	Block Valve	Leak	0	0.5	48	8	4	60.5	6.47×10^{-7}	5	3.24×10^{-6}	1.96×10^{-4}
DC-103	Packed Column	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	5	5×10^{-9}	1.83×10^{-7}
P-107	Pump	Leak	0	0.5	24	4	4	32.5	1.01×10^{-5}	5	5.05×10^{-5}	1.64×10^{-3}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	8.94×10^{-6}	5	4.47×10^{-5}	4.02×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	1	2.56×10^{-6}	2.30×10^{-5}
F-104	Reboiler	Leak in Coil	0	0.5	1	12	4	17.5	7×10^{-9}	5	3.5×10^{-8}	6.13×10^{-7}
		Burner Failure	0	0.5	0.5	8	4	13.0	4.6×10^{-5}	1	4.6×10^{-5}	5.98×10^{-4}

TABLE D-1. DETAILS OF THE CALCULATION OF THE AVAILABILITY OF THE HYDROLYSIS PROCESS (page 3 of 3)

Comp. No.	Component	Failure Mode	Down Time*						λ (Failure Rate)			υ
			t_1	t_2	t_3	t_4	t_5	$\sum_{i=1}^{5} T_i$ (hr)	Under Normal Conditions	Envir. Factor	Adjusted Failure Rate	(Component Unavailability)
C-102	Air Cooler	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3×10^{-9}	1.09×10^{-7}
		Blower Fails	0	0.5	0.5	4	4	9.0	3.809×10^{-6}	1	3.809×10^{-6}	3.43×10^{-5}
D-104	Reflux Drum	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	3	3.0×10^{-9}	1.10×10^{-7}
P-104	Pump	Leak	0	0.5	24	4	4	32.5	5.47×10^{-6}	3	1.69×10^{-5}	5.48×10^{-4}
		Internal Part Failure	0	0.5	0.5	4	4	9.0	4.98×10^{-6}	3	1.69×10^{-5}	1.34×10^{-4}
		Motor Failure	0	0.5	0.5	4	4	9.0	2.56×10^{-6}	1	2.56×10^{-6}	2.30×10^{-5}
C-106	Air Cooler	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	5	5.0×10^{-9}	1.83×10^{-7}
		Blower Fails	0	0.5	0.5	4	4	9.0	3.809×10^{-6}	1	3.809×10^{-6}	3.43×10^{-5}
T-103	Tank	Leak	0	0.5	24	8	4	36.5	1×10^{-9}	5	5×10^{-9}	1.83×10^{-7}
	Welded Pipe Connections P (10)	38 @ 3×10^{-9}	0	0.5	24	8	4	36.5	1.14×10^{-7}	10	1.14×10^{-6}	4.16×10^{-5}
	Welded Pipe Connections P (5)	25 @ 3×10^{-9}	0	0.5	24	8	4	36.5	7.5×10^{-8}	5	3.75×10^{-7}	1.37×10^{-5}
	Welded Pipe Connections P (3)	25 @ 3×10^{-9}	0	0.5	24	8	4	36.5	7.5×10^{-8}	3	2.25×10^{-7}	8.21×10^{-6}
	Gaskets or O-rings P (10)	4 @ $.53 \times 10^{-6}$	0	0.5	24	4	4	32.5	2.12×10^{-6}	10	2.12×10^{-5}	6.89×10^{-4}
	Gaskets or O-rings P (5)	4 @ $.53 \times 10^{-6}$	0	0.5	24	4	4	32.5	2.12×10^{-6}	5	1.06×10^{-5}	3.45×10^{-4}
	Gaskets or O-rings P (3)	4 @ $.53 \times 10^{-6}$	0	0.5	24	4	4	32.5	3.18×10^{-6}	3	9.54×10^{-6}	3.10×10^{-4}

* t_1 = sense time
t_2 = suit-up/flush
t_3 = isolate
t_4 = repair
t_5 = startup

immediately by the loss of pressure across the pump, and the searching time is virtually zero.

In estimating the time required for isolation and repair, the following "rule of thumb" was utilized. The time required for a similar task under nonhazardous conditions was estimated and then multiplied by a factor of three to account for the restrictions involved in working in a bulky protective suit--under very hazardous conditions.

11. Certain scenarios identified in the failure modes and effects analysis were judged to be highly unlikely and were not quantified. These scenarios were:

    (a) Clogging of coils in the furnace and reboilers with impurities and residue. This scenario was judged to be unlikely because of the presence of strong acids in these coils.

    (b) Clogging of bubble caps in the column. This scenario was judged unlikely because of the amount of residue necessary for clogging to occur as well as the presence of strong acids which will wash out the clogging materials.

    (c) Clogging of cooler coils. This scenario was judged to be unlikely as the liquids and vapors in these coils have undergone distillation and as such should be relatively pure.

    (d) Deterioration of packing in columns. This scenario could result in a sufficient restriction of flow through the packed columns to render their operation inefficient. This scenario was judged unlikely if the proper packing material in the columns is used.

    (e) Clogging or deterioration of static mixer. Clogging of the static mixer was judged unlikely due to the presence of strong acids. Deterioration of the mixer was judged to have a negligible influence on the system's performance and therefore was not considered to be a failure mode of consequence.

4. SUGGESTIONS/RECOMMENDATIONS BASED ON RELIABILITY ANALYSIS

1. It is recommended that pump P-105 have a redundant pump in parallel to accommodate decontamination and repair.
2. Replacement parts for system components should be kept on hand at the facility in order to expedite repairs.
3. It is recommended that the process components be designed in a modular construction so that subassemblies can be replaced/repaired easily. Adequate work space around the subassemblies should be provided to simplify disassembly while the operator is suited up in his bulky protective clothing.
4. Jackets on piping should be easy to remove and re-assemble. A transparent jacket would aid in the search for leaks.
5. A checklist should be developed for weekend inspections. This can be based on the failure modes identified in the failure modes and effects analysis.
6. It is recommended that redundant sensors be provided with the signals interpreted to minimize false alarms.

5. CALCULATION OF AVAILABILITY

λ_i = failure rate for component i

T_i = downtime for component i

MTBF = mean time between failures

$$= \frac{1}{\Sigma\lambda_i} = \frac{1}{9.38 \times 1^{-4}/\text{hr}} = 1066.1 \text{ hr} \qquad (\Sigma\lambda_i \text{ obtained from Table D-1})$$

MTTR = mean time to repair

$$= \frac{\Sigma\lambda_i t_i}{\Sigma\lambda_i} = \frac{1.93 \times 10^{-2}}{9.38 \times 10^{-4}/\text{hr}} = 20.58 \text{ hr}$$

A = availability

$$A = \frac{MTBF}{MTBF + MTTR} = \frac{1066.1 \text{ hr}}{1086.68 \text{ hr}} = .981$$

Scaled by corrosion factor α

$$\lambda_i \rightarrow \alpha\lambda_i$$

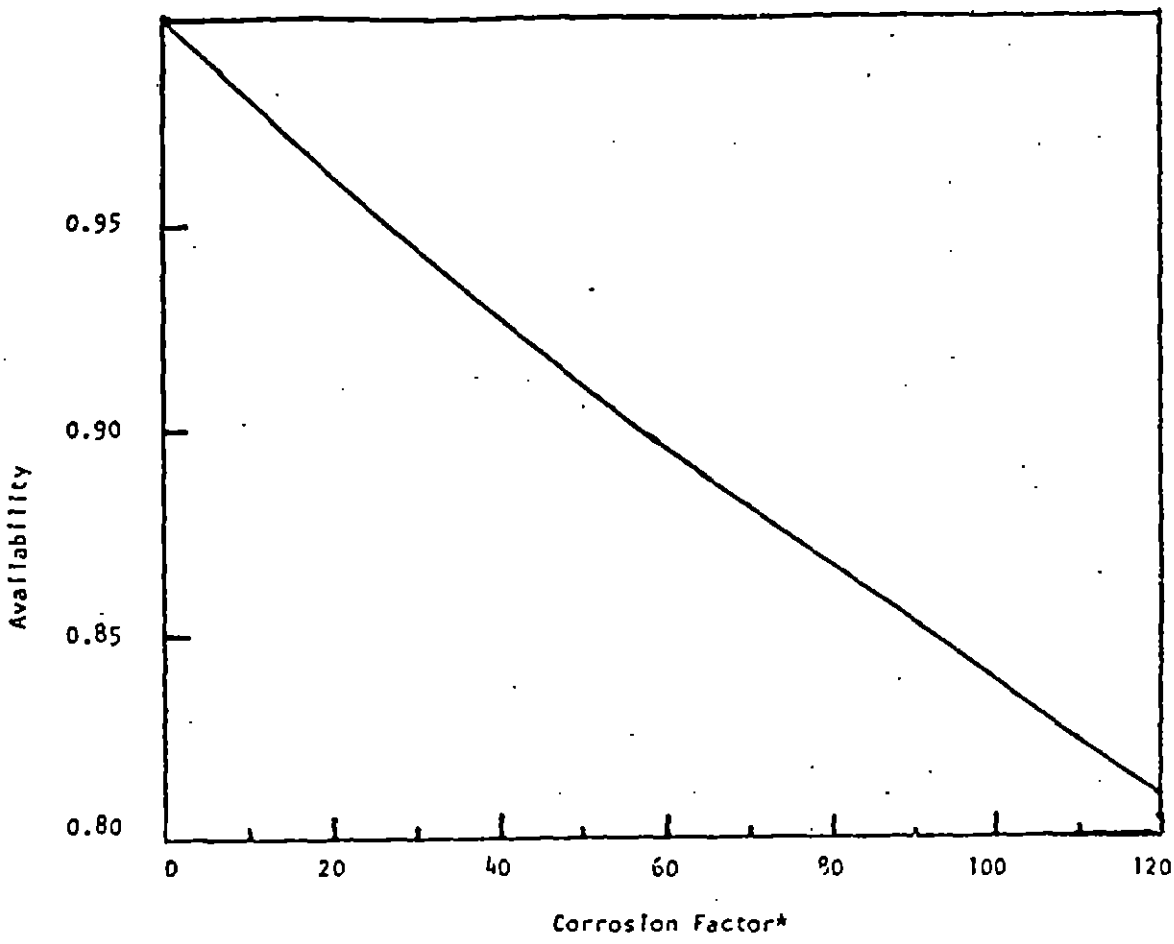
$$MTBF = \frac{1}{\Sigma\alpha\lambda_i} = \frac{1}{\alpha\Sigma\lambda_i} = \frac{1066.1 \text{ hr}}{\alpha}$$

$$MTTR = \frac{\Sigma\alpha\lambda_i t_i}{\Sigma\alpha\lambda_i} = \frac{\Sigma\lambda_i t_i}{\Sigma\lambda_i} = 10.58 \text{ hr}$$

$$A = \frac{MTBF}{MTBF + MTTR} = \frac{1066.1/\alpha}{1066.1/\alpha + 20.58} = \frac{1066.1}{1066.1 + \alpha 20.58}$$

The .981 factor is achieved with an $\alpha = 10$; Figure D-1 shows a plot of A versus α.

Figure D-1 illustrates the strong dependence of A on α. As α increases A decreases rapidly.



*A corrosion factor of 1 corresponds to a corrosion rate of 0.002 in/yr.

Figure D-1. Availability of the process for hydrolyzing GB as a function of corrosion factor.

DISTRIBUTION

Defense Technical Information Center Cameron Station Alexandria, VA 22314	12 copies
Defense Logistics Studies Information Exchange U.S. Army Logistics Management Center Fort Lee, VA 23801	2 copies
U.S. Army Toxic and Hazardous Materials Agency ATTN: DRXTH-ES Aberdeen Proving Ground, MD 21010	2 copies
U.S. Army Toxic and Hazardous Materials Agency ATTN: DRXTH-TE-D Aberdeen Proving Ground, MD 21010	10 Copies

END

DATE

FILMED

9-83

DTIC

Background Document I, Reference 13

MacNaughton, M.G., and J.H. Brewer, 1994, Environmental Chemistry and Fate of Chemical Warfare Agents, Final Report SWRI 01-5864, prepared for U.S. Army Corps of Engineers by Southwest Research Institute, San Antonio, Texas.

See Background Document B, Reference 37

Using
Dioxo-Ruthenium Porphyrins: A 1H NMR Investigation. 7) The Formation of
Pyrophophosphates in the Oxidation of Phosphonothiolates. 8) NMR of
Calixarenes. 9) Reactions of CW Agents in DS2. 10) 27Al and 11B NQR of
Ceramic Materials. 11) Solid-State NMR Study of Ambient Temperature
Aging of Carbon Black-Filled Rubbers.

300254

Document 716
DOCN 000052293
AD A259689
ACCN K300254
HARD 01
FICH
FILM
REST LIMITED
RPCI UNCLASSIFIED REPORT
CORP DEFENCE RESEARCH ESTABLISHMENT SUFFIELD RALSTON (ALBERTA)
SC 403104
TI Destruction and Waste Treatment Methods Used in a Chemical Agent
Disposal Project.
TICL (U)
NOTE Suffield Memorandum.
AUTH Mcandless, J M; Fedor, V
DATE 921000
PAGE 46
Abstract
1 This report describes the equipment and methods used to thermally
decontaminate scrap metal and destroy stockpiles of nerve agent, mustard
and lewisite chemical warfare agents. Mustard was destroyed by direct
incineration whereas the nerve agents and lewisite were chemically
neutralized. **The arsenic waste from the lewisite neutralization process
was stabilized in concrete for final disposal by landfilling.** The scrap
metal was incinerated and rendered suitable for recycling into metal
feedstock. Author.

502853

Document 180
DOCN 000023679
AD NONE
ACCN 502853
HARD 1
FICH
FILM
REST LIMITED

ACCN K300254
P 5&6

secondary combustion chamber (1200°C, 2.5s residence time) backed by a wet flue gas scrubbing system. This latter system recirculated caustic water through tandem venturi nozzles to remove acid gases and particulate matter prior to discharge of the flue gas to the main stack. Under normal operating conditions, this system consumed potable source water at 50 L/min and discharged recirculated water (scrubber blowdown) to holding tanks at 35 L/min. After analysis of the holding tank contents, the blowdown was then batch discharged to a polyethylene-lined lagoon to allow evaporation of water to the atmosphere.

During the winter of 1991 and at ambient temperatures below 0°C, bulk mustard was drained from pre-heated (20°C) 1-ton containers into heavy-walled cardboard boxes which were double-lined with polyethylene sheet. After allowing the mustard to freeze, the boxes were immediately transported to the incinerator facility in sealed metal cargo containers, off-loaded and processed via the rotary kiln solids waste feed system. This latter pneumatically-operated system was designed to accommodate single boxes of dimensions 45 cm x 45 cm x 200 cm for introduction into the kiln under closed conditions.

All neat mustard (3 tonnes) was destroyed in this manner as part of the incinerator trial burn program. The aged and thickened mustard (9 tonnes) contained in non-explosive ordnance was destroyed following approval of the trial burn results. During cold weather, ordnance items were punctured with small explosive perforating charges, sealed individually or in groups with adsorbent (vermiculite) in cardboard boxes and then incinerated. The thermally-decontaminated ordnance was recovered from the incinerator ash discharge system and stored outdoors to await final disposal.

Lewisite

As lewisite and its neutralization products contain arsenic, incineration of these materials potentially could produce arsenic-containing stack emissions and scrubber water.

Therefore, lewisite was destroyed by chemical neutralization using a special transportable apparatus (Figure 8) which could accept bulk liquid metered in from 1-ton cylinders. A three-step neutralization process was employed:

♦ conversion of lewisite to lewisite oxide (2-chlorovinyl arsine oxide) by addition of the agent to aqueous caustic hydrogen peroxide under controlled pH conditions;

♦ removal of excess peroxide reagent by circulating through a catalyst bed containing manganese dioxide, and

♦ conversion of lewisite oxide to arsenate and chloride salts under basic conditions with co-generation of acetylene. This step was carried out under nitrogen while bleeding off the acetylene to atmosphere.

After analysis to verify lewisite destruction efficiency, batches of the arsenic salt solution were mixed with sodium silicate and cement to produce a concrete-stabilized final waste product (see below, Stabilization). The cement mixture was cured in 210 L polyethylene barrels (Figure 9) which served as containers for the resulting product.

Contaminated Scrap

Empty 210 L drums were first shredded using a novel, self-contained transportable metal shredder (Figure 10) designed specifically for Project Swiftsure. Shredding was carried out primarily in cooler weather to minimize fugitive emissions from the shredding process. The shreds were packaged in cardboard boxes (approx. 100 kg of shreds per box) and fed into the incinerator via the solids waste feed system. The clean metal was then recovered from the incinerator ash discharge system and stored outdoors to await final disposal.

Vehicles

Scrap vehicles and metal parts which could not be shredded were subjected to a

FINAL

AGENT/DECONTAMINATION CHEMISTRY TECHNICAL REPORT

U.S. ARMY TEST AND EVALUATION COMMAND (TECOM) TECHNICAL SUPPORT

PHASE I

Prepared for

Environmental Quality Office
U.S. Army Test and Evaluation Command

Prepared by

David H. Rosenblatt, Ph.D.
Mitchell J. Small
Todd A. Kimmell
Andrew W. Anderson

Argonne National Laboratory

OCTOBER 19, 1995

FINAL

AGENT/DECONTAMINATION CHEMISTRY TECHNICAL REPORT

U.S. ARMY TEST AND EVALUATION COMMAND
(TECOM)
TECHNICAL SUPPORT

PHASE I

Table of Contents

APPENDICES

LIST OF TABLES

Appendix B

Appendix C

FINAL

AGENT/DECONTAMINATION CHEMISTRY TECHNICAL REPORT

U.S. ARMY TEST AND EVALUATION COMMAND
(TECOM)
TECHNICAL SUPPORT

PHASE I

FOREWORD

The U.S. Army intends to petition the State of Utah, in accordance with Rule R315 of the Utah Administrative Code and the Federal Resource Conservation and Recovery Act (RCRA), to delist certain F999 waste streams generated at the U.S. Army Dugway Proving Ground (DPG) from Utah's list of hazardous wastes. From 1991 to 1992, the Army conducted a program to gather, evaluate, and document all pertinent agent waste stream and supporting information that existed within Army records systems. This action resulted in the preparation of a series of test plans describing the demonstration testing program to be performed. In June of 1993, the Army met with the State of Utah, Department of Solid and Hazardous Waste, and presented its proposed approach to meeting the delisting requirements and filing a formal delisting petition. During this meeting, the State requested, among other things, that the Army provide a review of agent and agent decontamination chemistry.

This document is intended to fulfill the State's request in that regard. Its objective is to provide a comprehensive review of chemical agent chemistry, and the chemistry of decontamination processes for the agents H/HD, GB, GD, and VX. The document presents a review of the available literature, and identifies relevant information on agent and decontaminant by-products, additives, and breakdown products. It also addresses the ability of agents to reform following decontamination (referred to as toxic rebound), and discusses fate and transport of agents in the environment. Finally, the document presents a discussion on absorption and desorption from various types of materials.

As may be expected, the chemistry of agents and decontamination processes is technically complex. Despite this fact, it is important that the document be understandable to the regulator, and to the extent possible, to the general public. It has therefore been written in layman's terms; it is intended for an audience with a knowledge of general chemistry at the high school level. The document begins with a quick review of basic chemistry, as the basis for the ensuing discussions. Summaries of the technical information and what it means are also provided throughout the document.

The final draft of this document, dated June 6, 1995, was provided to the State of Utah, Department of Solid and Hazardous Waste for review and comment. In addition, on July 26-27, 1995, a conference was held at the State's offices in Salt Lake City, during which the basic tenets of the document were formally presented by the document authors. No written comments on the final draft document were received from the State, and while the State posed a number of questions during the formal presentation, no verbal comments were offered. In consideration, the Army believes that this final document satisfies the State of Utah's request or information on agent and agent decontamination chemistry.

FINAL

AGENT/DECONTAMINATION CHEMISTRY TECHNICAL REPORT

1.0 INTRODUCTION

The State of Utah, Department of Environmental Quality (DEQ), Division of Solid and Hazardous Waste (DSHW), has declared residues resulting from the demilitarization, treatment, cleanup, and testing of military chemical agents to be hazardous wastes. These residues have been designated as corrosive, reactive, toxic, and acute hazardous (Hazardous Waste No. F999). These residues are listed as hazardous waste by the State of Utah, and several other states, but they are not listed under the U.S. Environmental Protection Agency (EPA) regulations promulgated pursuant to the Resource Conservation and Recovery Act (RCRA), the primary law governing management of hazardous waste in the United States.

The RCRA regulations (40 CFR 260-280), the Utah Administrative Code (R-315), and other State hazardous waste programs list specific wastes as hazardous but allow generators to petition the regulator to "delist," if it can be demonstrated that such wastes are not hazardous. The U.S. Army Test and Evaluation Command (TECOM) believes that certain categories of F999 residues are not hazardous and has obtained assistance from Argonne National Laboratory (Argonne) to make the delisting demonstration.

The objective of this project is to delist chemical agent decontaminated residues resulting from materials testing activities and to delist a remediation residue (e.g., contaminated soil). To delist these residues, it must be demonstrated that the residues (1) do not contain hazardous quantities of the listed agents; (2) do not contain hazardous quantities of constituents listed in 40 CFR Part 261, Appendix VIII; (3) do not exhibit other characteristics that could otherwise define the residues as hazardous; and (4) do not fail a series of acute toxicity tests.

The TECOM Chemical Agent Decontaminated Residue and Remediation Waste Delisting Program (Delisting Program) will be implemented in a phased manner so that subsequent efforts can benefit from the documentation and experience obtained in earlier phases. The first phase of this program will focus on a subset of the F999 wastes generated at the U.S. Army Dugway Proving Ground (DPG), where the Army routinely tests the effects of military chemical agents and agent-decontamination procedures on numerous military items. This effort is identified as Phase I of the Delisting Program. Subsequent phases of this program will address other DPG chemical agent decontaminated residues and remediation wastes and similar residues at other installations.

The first major objective of Phase I is to conduct analytical method validation studies. The second major objective is to review and revise, as necessary, a series of test plans prepared previously to support the delisting effort and to develop a Quality Assurance/Quality Control (QA/QC) Plan. The test plans and QA/QC Plan will be implemented, and a Delisting Test Report will be prepared. These and other documents will form the basis of the Delisting Petition.

The Phase I effort will target two residues generated at DPG for delisting, including a decontaminated substrate residue and the decontamination fluid used to decontaminate that substrate. In addition, an agent-contaminated remediation waste (e.g., contaminated soil) will be addressed. These wastes will contain one

or more of the chemical agents H (HD), GB, GD, and VX. The Phase I effort is expected to last approximately 3.5 years, including the post-petition submittal period.

Analytical laboratories at DPG will be used to conduct agent and related analyses. Once samples have passed screening analyses for the absence of agents, they will be sent off-site to a commercial laboratory for RCRA testing. The analytical laboratory at DPG will only be able to support the Delisting Program during the winter months because the laboratory is expected to be busy performing analyses to support DPG's Installation Restoration Program (IRP) during the rest of the year. Hence, analytical method validation will be performed during the 1995-1996 winter period, and the delisting demonstration will be performed during the 1996-1997 winter period.

The objective of this document is to provide a comprehensive review of chemical agent chemistry and the chemistry of decontamination processes for the agents H/HD, GB, GD, and VX. It presents a review of the available literature and identifies relevant information on agent and decontaminant by-products, additives, and breakdown products. The document also addresses the ability of agents to reform following decontamination (referred to as toxic rebound) and discusses fate and transport of agents in the environment. Finally, it discusses absorption and desorption of agents from various types of materials. A glossary of symbols and acronyms is provided in Appendix A.

2.0 SCOPE AND CONCEPTS

2.1 Scope

This review considers chemical interactions between certain liquid decontamination systems and a selected group of chemical agents. The agents of interest are GB (sarin), GD (soman), VX, H (sulfur mustard), and HD (distilled sulfur mustard). These agents are tested at DPG to determine the interaction of chemical agents and decontaminants with military equipment and the efficacy of decontaminants for decontamination of contaminated materials.

In a typical experiment or test arrangement, a given amount of an agent would be applied to the surface of an engineered material (e.g., stainless steel or rubber). Then the surface would be contacted with a chosen liquid decontaminant under prescribed conditions for a specified time. At the end of that time, the decontaminating solution and the engineered material would be subjected to chemical and other analyses.

In addition to waste streams that result from the controlled decontamination of military equipment, DPG soil may have been contaminated through past operations or exercises with GB, VX, and H/HD (but historically not with GD) and through disposal of decontaminated materials. The contaminants in soils, assuming they were present initially, are expected to have undergone weathering, so they are no longer in the same chemical state as they were originally. It is therefore necessary to review what is known or believed regarding the environmental fate of GB, VX, and H/HD, as well as of other hazardous substances that might be present. This topic is reviewed separately in Appendix B of this document.

The interaction between polymeric substrate materials and the agents (the kinetics and equilibria of absorption and desorption) is discussed in Appendix C.

2.2 Concepts

This subsection discusses certain basic chemistry concepts to help the reader better understand the report.

Atoms, Molecules, and Ions. The simplest form of matter that the chemist deals with is the atom; the atom consists of a positively charged nucleus surrounded by negatively charged electrons. The nucleus, with virtually all the atom's mass, can contain within it a large number of units of positive charge, whereas each electron carries a single unit of negative charge. When atoms or groups of atoms have equal amounts of positive and negative charges, they are said to be "neutral." If there are more negative than positive charges, the (atom or) group of atoms is called an anion; if there are more positive charges, it is a cation. An element may exist as isolated atoms, for example, helium. Most elements, however, tend to combine in simple or complex ways with other atoms. Oxygen is illustrative; it is mainly present in the air, or dissolved in water, as a molecule consisting of two atoms, O_2. A small fraction of the world's elemental oxygen exists in groups of three oxygen atoms, O_3, known as ozone; this "trimer" of oxygen has properties much different from those of the more commonplace "dimer," O_2. An example of an anion is the hydroxide ion, the symbol for which is OH^-; the minus sign denotes the negative charge. The sodium ion, Na^+, is positively charged, and thus a cation. Sodium hydroxide, NaOH, contains an equal number of anions and cations.

The Structure of Molecules. Neutral molecules, generally speaking, are held together by "covalent" bonds, usually "single" bonds, but sometimes "double" or "triple" bonds, or other types. An example of the single bond is that in a chlorine molecule, Cl_2, or Cl-Cl (where the dash stands for a pair of electrons that constitute the covalent bond and that are shared between the two chlorine atoms). Carbon dioxide, O=C=O, has two double bonds. Organic compounds (compounds containing at least one carbon atom) can consist of a few or a great number of atoms linked mainly by covalent bonds.

Phases. The idea of phases is best expressed by example. If one tries to mix sand and water, the sand soon settles out as a solid phase, and the water becomes clear again as a liquid phase. If one attempts to dissolve oil in water, these separate into two liquid phases (though less rapidly if an emulsifying agent is added, as is often done with a salad dressing). A gaseous phase may be caused to dissolve in a liquid phase, as with a carbonated beverage, only to escape when the bottle is opened and the pressure reduced. One may dissolve sugar in hot tea; here two phases interact to become a single phase. The capacity of a substance to be accepted (dissolved) by a particular phase under a specified set of conditions, such as temperature and pressure, is referred to as the solubility of the substance in that phase under those conditions. When as much of the dissolved material (solute) is dissolved as the solvent can hold under the conditions, the solution is said to be "saturated".

Molecules and Ions in Solution. When a substance is dissolved in a solvent, its structure may be affected by the presence of the solvent. (The solvent is also affected by the dissolved substance — the solute.) One example is the tendency of a substance to dissociate. For example, when water is added to ethyl alcohol the concentration of ethoxide ions increases. This is simplistically expressed by the following:

$$C_2H_5OH \xrightleftharpoons{H_2O} C_2H_5O^- + H^+$$

Concentration in Solution. The concentration of a substance, in units of moles per liter, M, is expressed by enclosing the identifying symbol in square brackets (e.g., [GB]).

The pH of Aqueous (Water) Solutions. Neutral water (pH 7 at 25°C) has equal concentrations (denoted with square brackets) of hydroxide ions (OH^-) and protons (H^+), namely, $[OH^-] = [H^+] = 10^{-7}$ M. M stands for molar or moles per liter. If a solution is alkaline (basic), $[OH^-]$ exceeds 10^{-7}, with $[H^+]$ being correspondingly lower (and vice versa for an acidic solution), such that the ion product, $K_w = [OH^-] \times [H^+]$, is always 10^{-14} M^2. In simple terms, one defines pH as ($-\log [H^+]$); the pH of a neutral solution would be 7. Any solution with a pH above 7 is alkaline; that with a pH below 7 is acidic. Because pH is on a logarithmic scale, a drop of one unit in pH indicates a 10-fold increase in acidity (hydrogen ion activity). The pH is often an important determinant of chemical reactivity in aqueous solutions.

The pK_a of an Acidic Solute. If a solute, generically symbolized by HA, dissociates in water to furnish protons, i.e., $HA \rightleftharpoons H^+ + A^-$, we may express the degree to which this takes place as $K_a = [H^+][A^-]/[HA]$. The greater the magnitude of K_a, the more acidic HA is said to be. The related term, $pK_a = -\log K_a$, is the way in which the property is usually expressed. The smaller pK_a, the more acidic is HA. The pH at which $[HA] = [A^-]$ is approximately equivalent to the pK_a.

Chemical Reactions, Mechanisms. Chemical reactions typically involve the breaking and making of chemical bonds, or the loss or gain of electrons. The step or steps that occur in such a process are known, collectively, as a reaction mechanism. Frequently, the parts of a molecule that do not change during the course of a reaction are represented generically in chemical shorthand by a symbol such as R. Thus the hydrolysis (cleavage by water) of chloromethane (CH_3Cl), chloroethane (C_2H_5Cl), or other chlorinated hydrocarbons could be represented generically by the following:

$$R\text{-}Cl + H_2O \longrightarrow R\text{-}OH + HCl$$

Here, a bond between a carbon in the group "R" and a chlorine atom was broken, and a bond between that carbon and part of a water molecule (i.e., OH) was formed. Hydrolysis reactions take many forms. They are frequently catalyzed (accelerated) by acid (such as H^+) or base (such as OH^-), but the range of possible catalysts is quite broad and includes such entities as soil minerals and enzymes.

Oxidation-reduction (redox) reactions are characterized by the loss and gain of electrons or of electron-rich atoms like oxygen or chlorine. As an example of electron transfer, the reaction between iron (Fe) and chlorine (Cl_2) to produce ferrous chloride requires the transfer of two electrons from the iron to a chlorine molecule:

$$Fe + Cl_2 \longrightarrow Fe^{++} + 2\,Cl^-$$

The superscript + or – signs denote units of nuclear or electronic charge. The reaction of ozone (O_3) with sulfur dioxide exemplifies the transfer of an oxygen; the sulfur dioxide is oxidized to sulfur trioxide, and the ozone is reduced to O_2 ("dioxygen"):

$$SO_2 + O_3 \longrightarrow SO_3 + O_2$$

The reaction of sulfur dioxide with chlorine to form sulfuryl chloride is also considered an oxidation, with chlorine being the oxidant:

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

Reagents. A reagent is a substance introduced into a system to react with other substances. Conventionally, all reagents are "reactants," but the reverse is not necessarily true.

Nucleophiles and Electrophiles. The term "nucleophile" refers to a class of reagents that have a special affinity for centers of positive charge other than H^+ (such as the phosphorus atoms in the nerve agents); hypochlorite ion (ClO^-) and hydroperoxide ion (HOO^-) are nucleophiles. At the opposite extreme, many oxidizing agents, such as Cl_2, are called "electrophiles" because they seek out accessible electrons.

Kinetics. This term encompasses various factors influencing the speed with which chemical reactions take place. In some reactions, all the molecules or ions that can find each other react almost as soon as the reacting materials are mixed; in other cases, reactions proceed at an extremely slow pace, with few encounters producing a chemical change. For a chemical reaction to occur, the reactants have to be sufficiently close to each other, be in the correct orientation towards each other, and possess sufficient energy to overcome forces of repulsion that might keep them from reacting. Allowing for exceptions, one may say that (1) the higher the concentration of each reactive species, the higher the reaction rate, and (2) the higher the temperature, the faster the reaction (because the reactants possess more kinetic energy).

Half-Life of a Reaction. As a reaction proceeds, the starting materials (reactants) get used up. If one reactant is originally in excess, its concentration ratio increases with time. Eventually, only the reactant that was in excess remains. A large excess of one reactant may be used intentionally, even at the beginning of the process. Often, when some of the reagents are in large excess, the time interval for any given concentration of the reactant not in excess to fall to half that concentration is constant. For example, the initial concentration of the low-concentration reactant is 800 mg/L (milligrams per liter) and decreases in 10 min to 400 mg/L. In the next 10 min it falls to 200 mg/L. The "half-life" of the reaction in this example is 10 min. If such a reaction is allowed to proceed for seven half-lives, the low-concentration (or "limiting") reactant will have been diminished to less than 1% of its original concentration within 70 min in the present example. Study of the reaction kinetics may make it possible to select conditions under which the concentration of the reactant of concern may be decreased to a desired level in a given length of time.

Multistep Reactions. Often, one deals with a sequence of reactions rather than with a single reaction. One such type of sequence is conceptually visualized as:

$$\text{(1) } A + B \longrightarrow C \text{ and possibly other products}$$
$$\text{(2) } A + C \longrightarrow D \text{ and possibly other products}$$
$$\text{(3) } A + D \longrightarrow E \text{ and possibly other products}$$

And so forth

If the amount of compound A is much larger than that of compound B and step (1) is rapid compared to step (2), compound C can accumulate before being eventually consumed. If the initial quantity of compound A is equal to that of compound B and step (2) is very fast compared to step (1), then only half of compound B will be consumed and compound C will not accumulate. Such examples illustrate the complexity and variety of phenomena associated with multistep reactions. Moreover, the same reagents may produce two or more sets of products (in competing reactions).

Role of Chemical Analysis. To deduce the mechanisms and determine the kinetic factors used to predict the kinds and amounts of reaction products for chosen conditions, the chemist must analyze the compositions of experimental reaction mixtures at intervals during the course of reaction. Sometimes this can be done with essentially noninvasive techniques such as spectrophotometry, nuclear magnetic resonance (NMR) spectrometry, or the measurement of pH. At other times, it may be necessary to stop ("quench") the reaction by chilling or neutralizing a sample of the reaction mixture before conducting complex manipulations, such as chromatography. The choice of sensitive analytical tools has increased dramatically over the past 50 years, but some of the most valuable analytical information about the reactions of chemical agents is about half a century old.

Decontamination. Decontamination refers to the effective removal of a contaminant, such as a chemical agent, from a given medium. Decontamination may consist primarily of physical removal, involving transfer of the contaminant to another medium without altering its chemical identity. In this review, however, attention is paid to the chemical reactions that convert the organic contaminants of interest to compounds of quite different identities and properties and, in some cases, to inorganic end-products.

Solubility. Solubility is an important determinant of the feasibility of conducting chemical decontamination under a given set of conditions. Chemical reactions occur most readily when the reactants are dissolved in the same phase. If a chemical agent is not rapidly dissolved in a liquid decontaminant, the reaction is confined to the interface between phases and is usually a rather slow process. Low solubility tends to be a particular problem for decontaminating sulfur mustard (H/HD) with aqueous decontaminants.

3.0 PHYSICOCHEMICAL PROPERTIES OF THE AGENTS OF CONCERN

Selected properties of the agents addressed in this document are recorded in Tables 1-4 and other information is presented and discussed in the text.

3.1 Physicochemical Properties

3.1.1 Vapor Pressure (P)

Vapor pressure is the pressure at which a liquid (or solid) and its vapor, at a given temperature, are in equilibrium. The vapor pressure of a compound is commonly given for the state — solid or liquid — in which the substance is likely to occur under ambient conditions, typically 25°C. If vapor pressures have been determined for a range of temperatures, the data may be presented as the constants of Antoine equations, $\log P = A - B/(C + t)$, where the temperature, t, is in degrees Celsius (°C). (Note that the equation is equivalent to a Clausius-Clapeyron equation when C = 273.16.) Units for the value P are in torr (mm of mercury). A high vapor pressure indicates that a substance can easily evaporate if exposed to the atmosphere.

3.1.2 Log Octanol/Water Partition Coefficient

The octanol/water partition coefficient, K_{ow}, is the ratio between the concentration of the compound of interest in the octanol phase to its concentration in the aqueous phase when the two phases are in equilibrium. This

parameter is commonly expressed as its logarithm, log K_{ow}. Though K_{ow} is an indicator of relative lipophilicity (affinity towards fats), it is primarily used as a starting point to estimate such properties as bioconcentration factors, aqueous solubilities, and coefficients of adsorption to soil and sediment. Experimental values for numerous compounds have been reported for log K_{ow}, and these should be used if they are available and reliable. Otherwise, values are calculated from fragment constants and structural factors, or from other solvent-water partition coefficients through linear regression equations (Lyman et al. 1990). High values of K_{ow} (or log K_{ow}) indicate that a substance will tend to concentrate in soil organic matter or in fatty tissue rather than in water.

3.1.3 Henry's Law Constant (K_H)

The Henry's Law constant, here applied to the aqueous solutions in contact with air, is a measure of the ratio of the concentration of a compound in the gaseous state to its concentration (as a nonionic species) in solution. K_H is commonly estimated as a ratio of vapor pressure at a particular temperature to the saturation solubility at the same temperature. For most of the data presented below, the following equation was used to calculate K_H from the vapor pressure P (torr or mm of mercury) of the pure solute, gram molecular weight (MW), and solubility S (mg/L) of the solute in the solvent:

$$K_H \text{ (atm•m}^3\text{/mol)} = (P \times MW)/(S \times 760)$$

Because environmental concerns are usually related to exposures to low concentrations of potentially toxic materials, namely to the Henry's Law constant at infinite dilution, this kind of estimation is most valid for compounds of low solubility. It cannot be used at all for substances miscible in all proportions (such as GB, in which case the ratio of a measured pair of concentration values at equilibrium was used for the calculation).

The higher the value of K_H, the more an organic solute will tend to volatilize from an aqueous solution.

If K_H is expressed in torr M^{-1}, it may be converted to (atm•m^3/mol) through division by 760,000; also, if K_H is expressed in the latter units, multiplication by the constant 40.88 mol/(m^3•atm) converts it to the dimensionless form for 25°C.

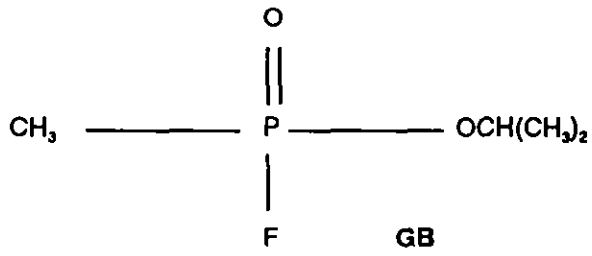
3.1.4 Soil Organic Carbon/Water Partition Coefficient (K_{oc})

The soil organic carbon/water partition coefficient, K_{oc}, is defined as (μg adsorbed chemical per g organic carbon)/(μg chemical per mL of solution). Estimating the actual partition coefficient, K_d, of a chemical between soil and water from this value is based on the assumption that the soil's organic content is the only determinant of the sorption of a compound from water to soil. Thus, $K_d = f_{oc} \times K_{oc}$, where f_{oc} is the fraction of organic carbon in the soil. The organic *matter* content, as opposed to organic *carbon* content, may be converted to f_{oc} by multiplying it by 0.58. Log K_{oc} was calculated from log K_{ow} by the following equation (Lyman and Loreti 1987):

$$\log K_{oc} = 0.824 \log K_{ow} + 0.328$$

The greater the value of log K_{oc}, the greater the tendency of a substance will be to stick to the organic matter in soil and not to migrate with the groundwater or to vaporize into the air.

3.2 GB (Sarin or Isopropyl Methylphosphonofluoridate); CAS Reg. No. 107-44-8

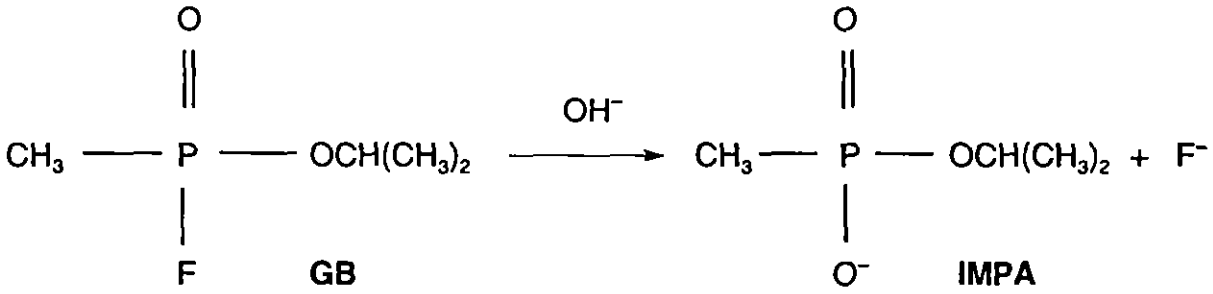


GB

GB, or sarin, is a relatively nonpersistent nerve agent. For instance, at 25°C and a loading of 3.33 mg/cm^2, it persisted on concrete for only 2 h (Cooper 1990). Experiments showed 99% disappearance of GB from pulverized or intact concrete in 30 min or less (Carpenter and Hill 1988). It evaporates at about the same rate as water (Headquarters, Departments of the Army, Navy, and Air Force 1990). Its hydrolytic half-life is longest in the pH range of 4 to 6, about 160 h at pH 5 and 25°C, and decreases outside that range in either more alkaline or more acidic solutions (Clark 1989). The second order rate constant for hydroxyl ion–catalyzed hydrolysis is:

$$\log k_2\ (M^{-1}\ min^{-1}) = 9.8507 - (1{,}985.4/T[K]) \qquad \text{(Demek et al. 1970)}$$

where



This gives a value of 1,543 $M^{-1}min^{-1}$ at 25°C. Hence, the estimated pseudo-first order rate constant at pH 10 is 0.1543 min^{-1}, and the half-life at that pH is 5 min. Hydrolysis of GB produces two far less toxic products, hydrofluoric acid and isopropyl methylphosphonic acid (IMPA). In the presence of a base such as hydroxyl ion, these acids are deprotonated to the corresponding anions. When large amounts of GB are added to distilled water, the observed hydrolysis rate constant first decreases but increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect.

In addition to the environmentally relevant data in Table 1, the following temperature relationships were reported for GB:

Vapor pressure, log P (torr) = 7.48160 - 1,773.82/(227.9 + t [°C]) (Samuel et al. 1983)

Density, d = 1.1182 - (0.00118 t[°C]) (Samuel et al. 1983)

To summarize, GB is rather volatile, infinitely soluble in water, and subject to both acid- and base-catalyzed hydrolysis.

Because of the sensitivity of GB to hydrolysis and to acid-catalyzed decomposition, N,N'-diisopropyl-carbodiimide and/or tributylamine have been added as stabilizers for weapons-grade GB. The requirement for N,N'-diisopropylcarbodiimide in 1.50% excess was spelled out in specification documents (Edgewood Arsenal 1968; U.S. Army 1969); according to these documents, the GB had to be at least 93% pure, and up to 0.5% methylphosphonic difluoride would be an acceptable component. Tributylamine is referred to by Epstein et al. (1977) and in specifications (U.S. Army 1969). GB may also contain some diisopropyl methylphosphonate (DIMP) as an impurity. N,N'-Diisopropylurea is a hydrolysis product of N,N-diisopropyl carbodiimide.

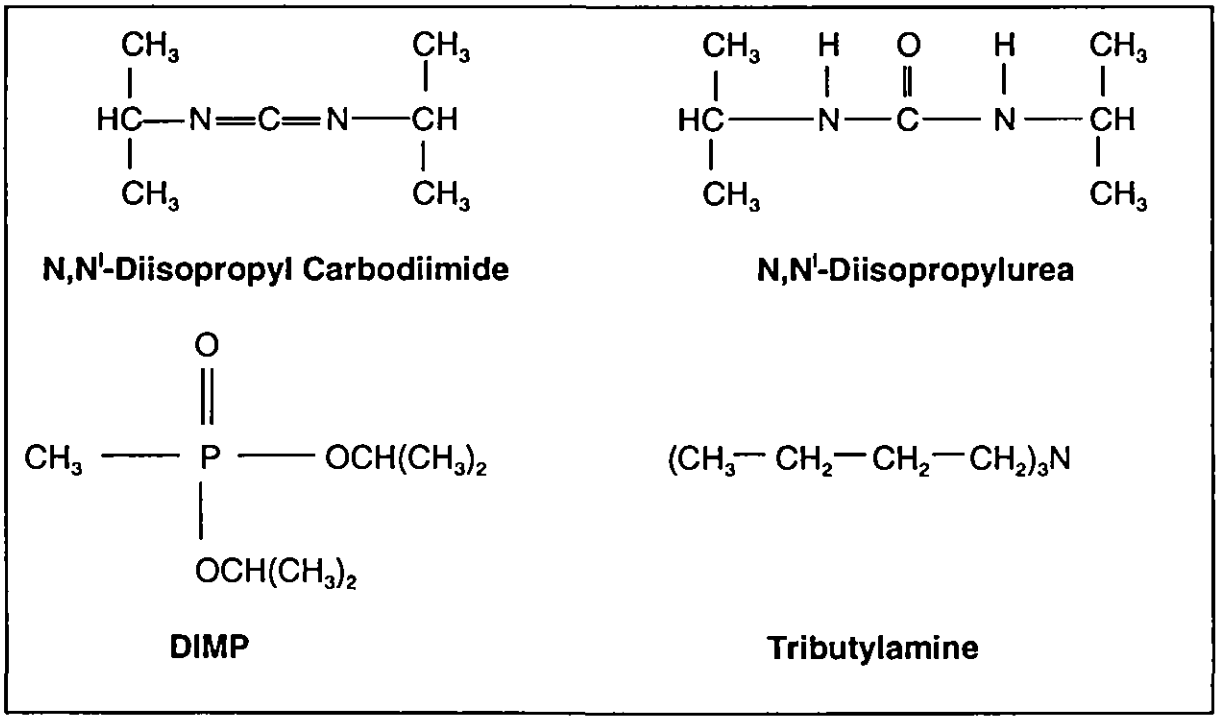


Table 1. Environmentally Relevant Properties of GB

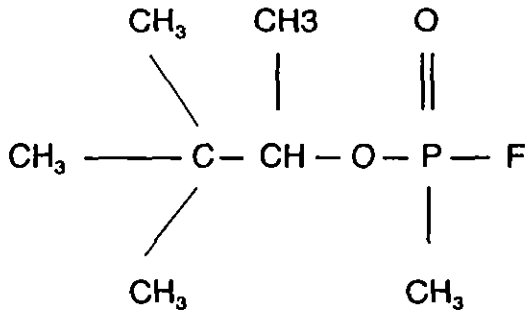
Property	Data	Data Quality	Reference
Empirical Formula	$C_4H_{10}FO_2P$	Not Applicable	
Molecular Weight (MW) (g/mol)	140.1	Not Applicable	
Density (g/mL)	1.0887/25°C	Good	Samuel et al. (1983)
Melting Point (°C)	-56.9	Fair	Samuel et al. (1983)
Boiling Point (°C)	157.8	Good	Samuel et al. (1983)
Heat of Vaporization (cal/g)	80.66	Good	Samuel et al. (1983)
Vapor Pressure at 25°C (torr)	2.94	Good	Samuel et al. (1983)
Log K_{ow}	0.15[a]	Poor	Britton and Grant (1988)
Aqueous Solubility (g/L)	Miscible in all proportions	Good	Headquarters, Department of the Army, Navy and Air Force (1990)
K_H (atm•m^3/mol)	4.0 x 10^{-7}/25°C	Poor	Preston and Starrock (1993)[b]
Diffusion Coefficient (air) (cm^2/s)	0.061/25°C	Fair	Samuel et al. (1983)
Log K_{oc}	0.45	Poor	[c]

[a] The authors of the present report estimated log K_{ow} by regression equations (see Section 3.1.2) involving distribution coefficients for four solvents (Rosenthal et al. 1956), with log K_{ow} values ranging from 0.12 to 1.30 and a mean of 0.74.

[b] Based on estimated vapor pressure of 0.136 kPa for 0.1 mole fraction (about 3.34 M) of GB in water, K_H = 0.00134 atm/(3,340 mol/m^3) from Fig. 2.

[c] Authors' estimate (see Section 3.1.4). Small (1984) estimated 1.8.

3.3 GD (Soman or Pinacolyl Methylphosphonofluoridate); CAS Reg. No. 96-64-0



GD

GD, or soman, was designed as a somewhat more persistent nerve agent than GB. It evaporates at about one-fourth the rate of water. Its hydrolytic half-life is longest in the pH range of 4 to 7, about 144 h at pH 5 and 20°C, and increases outside that range in either more alkaline or more acidic solutions (Clark 1989). The observed hydrolysis rate constant at 25°C, exclusive of buffer effects (Healy 1948), is k_{obs} (h^{-1}) = 0.0047 + 33[H_3O^+] + 5x10^4[OH^-]. Hydrolysis of GD produces two far less toxic acids as products, hydrofluoric and pinacolyl methylphosphonic acids. In the presence of a base such as hydroxyl ion, these acids are deprotonated to the corresponding anions. When large amounts of GD are added to distilled water, the observed hydrolysis rate constant first decreases but increases once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect.

In addition to the environmentally relevant data in Table 2, the following temperature relationships were reported for GD:

Vapor pressure, log P (torr) = 7.47060 - 1,903.10/(216.9 + t[°C]) (Samuel et al. 1983)

Density, d = 1.0456 - (0.00093 t[°C]) (Samuel et al. 1983)

In conclusion, GD may be compared to GB in its behavior but is considerably less water soluble and less volatile.

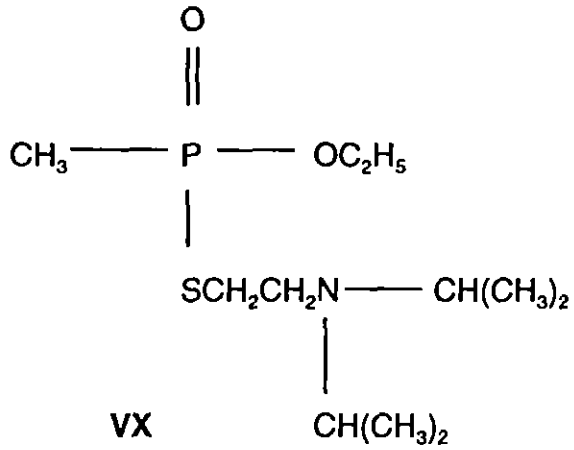
Table 2. Environmentally Relevant Properties of GD

Property	Data	Data Quality	Reference
Empirical Formula	$C_7H_{16}FO_2P$	Not Applicable	
Molecular Weight (MW) (g/mol)	182.18	Not Applicable	
Density (g/mL)	1.0223/25°C	Good	Samuel et al. (1983)
Melting Point (°C)	-42	Fair	Samuel et al. (1983)
Boiling Point (°C)	197.8	Good	Samuel et al. (1983)
Heat of Vaporization (cal/g)	72.5	Good	Samuel et al. (1983)
Vapor Pressure at 25°C (torr)	0.40/25°C 0.274/20°C	Good Good	Samuel et al. (1983) [a]
Log K_{ow}	1.02[b]	Poor	Britton and Grant (1988)
Aqueous Solubility (g/L)	34/0°C 21/20°C	Fair Fair	Edgewood Arsenal (1974) Samuel et al. (1983)
K_H (atm•m^3/mol)	3.1 x 10^{-6}/20°C	Poor	Authors estimate (see Section 3.1.3).
Diffusion Coefficient (air) (cm^2/s)	0.047/25°C	Fair	Samuel et al. (1983)
Log K_{oc}	1.17	Poor	Authors' estimate (see Section 3.1.4).

[a] From the Antoine equation (see text).

[b] The present authors estimated log K_{ow} by regression equations (see Section 3.1.2), using distribution coefficients for two solvents (Rosenthal et al. 1956) to obtain log K_{ow} = 1.79 and 1.60.

3.4 VX (O-Ethyl S-[2-Diisopropylaminoethyl] Methylphosphonothioate); CAS Reg. No. 50782-69-9



VX

VX, a nerve agent that penetrates skin easily, is more persistent than G-agents because of its low vapor pressure; its evaporation rate is about 1/1,500 that of water (Headquarters, Departments of the Army, Navy, and Air Force 1990). Nevertheless, the literature indicates that, most conservatively, 90% of VX applied to soil would be lost in 15 days (Small 1983). When 0.25-inch concrete coupons were spiked with 1.8 mg/g of VX and allowed to stand for 2 h, no VX could be recovered from the headspace after heating at 140°C (Carpenter and Hill 1988). VX hydrolysis rates tend to be slower than those of the G-agents; thus, at pH 10 and 25°C, the half-life in water is 2,432 min (converted data from Epstein et al. [1974]), compared to 5 min for GB. At pH 5 and 25°C, the half-life was reported as 2,342 h (Clark 1989). VX is not subject to acid-catalyzed hydrolysis but does undergo water-mediated and hydroxyl ion-catalyzed hydrolysis. According to Epstein et al. (1974), water-catalyzed hydrolysis below pH 7 and alkaline hydrolysis above pH 10 result in P-S cleavage, to give ethyl methylphosphonic acid (EMPA) and 2-diisopropylaminoethanethiol (DESH). Complex mixtures of hydrolysis products are formed in the pH range 7-10; these involve ethoxy cleavage from the phosphorus as well as C-S and P-S cleavage at the sulfur (Epstein et al. 1974). Some of the products are considered toxic. Thus, bis(2-diisopropylaminoethyl) disulfide (EA 4196), formed by air oxidation of the primary cleavage product DESH, is believed to be a powerful vesicant, similar in effect to mustard gas (Small 1983). The product of ethoxy cleavage, S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA 2192), is comparatively stable towards hydrolysis and almost as toxic as VX (Sage and Howard 1989). Contrary to Epstein, Yang et al. (Section 5.1.2) show that ethoxy cleavage occurs significantly at pH levels much higher than 10.

In addition to the environmentally relevant data in Table 3, the following temperature relationships were reported for VX:

$$\text{Vapor pressure, log P (torr)} = 7.28100 - 2{,}072.10/(172.5 + t[^\circ C]) \quad \text{(Samuel et al. 1983)}$$

$$\text{Density, d} = 1.0290 - (0.00083\ t[^\circ C]) \quad \text{(Samuel et al. 1983)}$$

The pK_a of protonated VX at 25°C has been given as 8.60 (Epstein et al. 1974) or 9.1 (Demek et al. 1970). VX is much more soluble in the protonated form (below a pH of about 7 or 8), than it is in the unprotonated (free base) form.

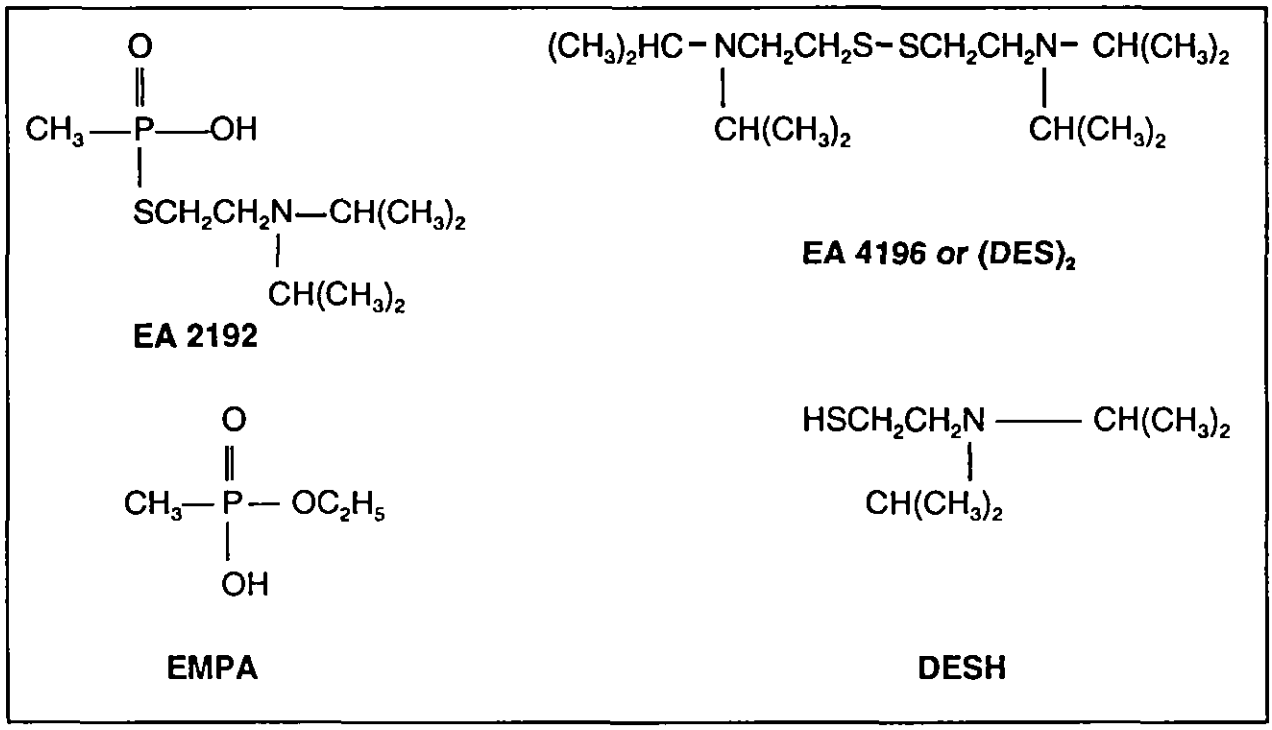
Table 3. Environmentally Relevant Properties of VX

Property	Data	Data Quality	Reference
Empirical Formula	$C_{11}H_{26}NO_2PS$	Not Applicable	
Molecular Weight (MW) (g/mol)	267.38	Not Applicable	
Density (g/mL)	1.0083/25°C	Good	Samuel et al. (1983)
Melting Point (°C)	-50	Fair	Samuel et al. (1983)
Boiling Point (°C)	298.4	Good	Samuel et al. (1983)
Heat of Vaporization (cal/g)	80.8	Good	Samuel et al. (1983)
Vapor Pressure (torr)	6.2×10^{-4}/25°C	Good	Samuel et al. (1983)
Log K_{ow}	2.36 (estimate) 2.09 (estimate) 1.992 (estimate)	Poor Poor Poor	Britton and Grant (1988) Small (1984) Sage and Howard (1989)
Aqueous Solubility (g/L)	30/25°C	Fair	Edgewood Arsenal (1974)
K_H (atm•m^3/mol)	7.2×10^{-9}/25°C	Poor	Authors estimate (see Section 3.1.3)
Diffusion Coefficient (air) (cm^2/s)	0.034/25°C	Fair	Samuel et al. (1983)
Log K_{oc}	1.18[a]	Poor	Sage and Howard (1989)

[a] *Small (1984) estimated a value of 2.5.*

In summary, VX is quite persistent and not very water soluble in basic aqueous solution but much more so in acidic solution. It is hydrolyzed by base, and more slowly in neutral or acidic solution, but not nearly as rapidly as GB or GD under comparable conditions. Complex mixtures of hydrolysis products are formed.

Because of the sensitivity of VX to hydrolysis, diisopropyl carbodiimide or dicyclohexyl carbodiimide have been added as stabilizers for weapons-grade VX (U.S. Army 1964; Durst et al. 1988).



3.5 HD/H (Sulfur Mustard or Mustard Gas or Bis[2-chloroethyl] Sulfide); CAS Reg. No. 505-60-2

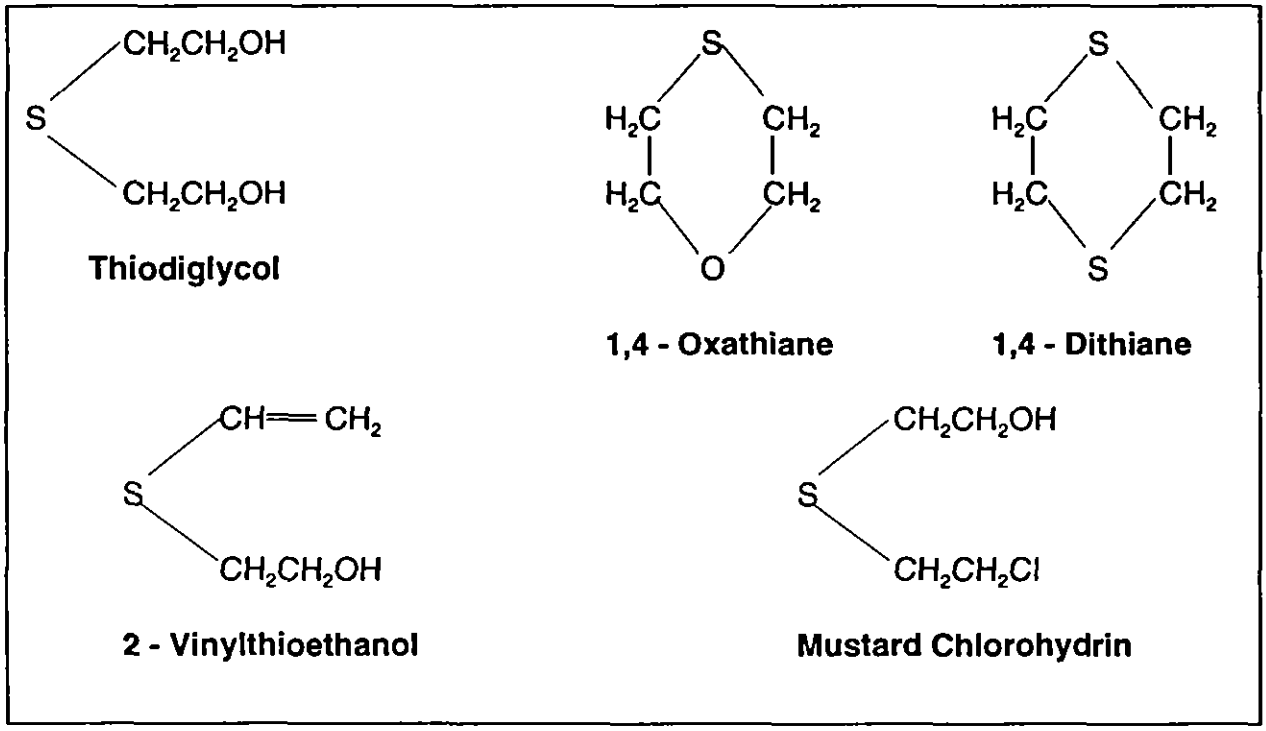
$$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$$

H differs from HD in that H contains certain impurities normally absent from HD; however, there is no standard composition for H.

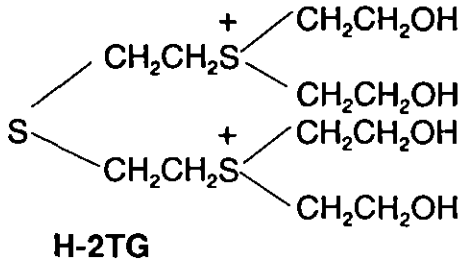
3.5.1 HD (Distilled Mustard or Distilled Sulfur Mustard)

Virtually all available physicochemical information on what is commonly known as "mustard gas," a blister agent, has been determined on the relatively pure material, HD. This compound has a low solubility in water and a low rate of solution. According to Dacre and Burrows (1988), a pool of HD at the bottom of a water body,

relatively undisturbed by currents, would diminish in depth by 1 cm every 100 days at 20°C. For these reasons, HD is difficult to decontaminate by aqueous hydrolysis (to thiodiglycol) despite the relatively high first-order rate constant of the reaction once the HD is in solution (see Section 5.1.3). As discussed in Section 3.5.2, large-scale hydrolysis in the presence of lime (to neutralize the hydrochloric acid that was produced) gave mainly thiodiglycol; however, significant amounts of 1,4-oxathiane, 1,4-dithiane, 2-vinylthioethanol, and in some cases mustard chlorohydrin were found in the hydrolysate, along with lesser amounts of other organics (D'Agostino and Provost 1985). Sludge formed in this process contained a number of organic compounds, among them bis(2-chloroethyl) trisulfide; many of the products were unidentified (D'Agostino and Provost 1985).



The gas chromatographic analytical procedures used in the foregoing work (D'Agostino and Provost 1985) would not have detected ionic products such as



H-2TG

This ion, as determined by NMR spectrometry, was the main organic constituent of the aqueous phase of a two-phase mixture of equal volumes of HD and water that had been allowed to stand for 2 months; ions of this type retain much of the toxicity of mustard, including its vesicancy (Yang et al. 1987). Thus, reaction of HD with limited volumes of water can result in the loss of HD without corresponding loss of toxicity.

The fact that bulk HD (or H) can persist deep in the soil or under relatively quiescent water for years may be due to the formation of oligomeric degradation products of limited hydrolysis, such as that shown above; presumably these coat the surface of the HD mass. In another sort of scenario, HD films on or near the soil surface would volatilize or hydrolyze within about 3 weeks (Small 1984). Under calm dry conditions at 0°C, an original heavy soil loading of 50,000 mg/m^2 is predicted to decay to 33 mg/m^2 in 1,530 h, some 2 months; the time is reduced to 41.5 h at 25°C (Small 1984). When 0.25-inch concrete coupons were spiked with 1.8 mg/g of HD and let stand for 24 h, no HD could be recovered from the headspace after heating at 140°C (Carpenter and Hill 1988).

In addition to the environmentally relevant data in Table 4, the following temperature relationships were reported for HD:

$$\text{Vapor pressure, log P (torr)} = 7.4749753 - 1{,}940.711/(204.6712 + t[^\circ C]) \quad \text{(Penski1993)}$$

$$\text{Density, d} = 1.2954 - (0.00107\ t[^\circ C]) \quad \text{(Samuel et al. 1983)}$$

To conclude, mustard agent (H or HD) is fairly persistent. It is difficult to dissolve in water but, once dissolved, it is quick to hydrolyze to thiodiglycol. Large masses of mustard can become coated with intermediate hydrolysis products that tend to prevent further hydrolysis and preserve the agent for long periods.

3.5.2 H (Impure Sulfur Mustard)

The symbol H has probably been used in various ways to designate unpurified (in particular undistilled) mustard made by any process and to refer to distilled mustard (HD) that has been stored under conditions permitting significant degradation. The latter could be caused by the presence of oxygen or water or simply by thermal decomposition over time. Storage in steel containers, especially in conjunction with other factors (e.g., moisture), has probably contributed to such degradation. H is likely to be more viscous than HD and to contain suspended solids.

Mustard was synthesized for military use mainly by the Levinstein process (Fuson et al. 1946a) and distillation was not initially used but was later adopted to improve the agent's storage stability. The Levinstein process is shown in the simplest terms as a reaction between sulfur monochloride and ethylene:

$$S_2Cl_2 + 2\ CH_2{=}CH_2 \longrightarrow \underset{\textbf{Mustard}}{Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + \underset{\textbf{Elemental Sulfur}}{S}$$

Table 4. Environmentally Relevant Properties of HD

Property	Data	Data Quality	Reference
Empirical Formula	$C_4H_8Cl_2S$	Not Applicable	
Molecular Weight (MW) (g/mol)	159.08	Not Applicable	
Density (g/mL)	1.2685/25°C	Good	Samuel et al. (1983)
Melting Point (°C)	14.445	Good	Penski (1993)
Boiling Point (°C)	217.5	Good	Samuel et al. (1983)
Heat of Vaporization (*cal/g*)	94.3	Good	Samuel et al. (1983)
Vapor Pressure (torr)	0.082/22°C[a]	Good	Samuel et al. (1983)
	0.1059/25°C[a]	Good	Samuel et al. (1983)
Log K_{ow}	1.37	Good	[b]
	2.026	Fair	Sage and Howard (1989)
Aqueous Solubility (g/L)	0.92/22°C	Fair	Edgewood Arsenal (1974)
K_H (atm•m^3/mol)	1.87×10^{-5}	Fair	Authors' estimate (see Section 3.1.3).
	2.57×10^{-5}	Fair	Sage and Howard (1989)
Diffusion Coefficient (air) (cm^2/s)	0.060/25°C	Fair	Samuel et al. (1983)
Log K_{oc}	2.0-2.1	Poor	Sage and Howard (1989)

[a] From the Antoine equation (see text).

[b] Authors' estimate from fragment constants (see Section 3.1.2) in agreement with Small (1984) and the U.S. Environmental Protection Agency (1986).

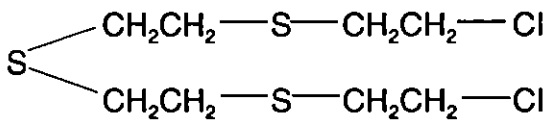
The excess sulfur in Levinstein mustard may react in various ways to form polysulfide impurities, such as the trisulfide Cl-CH_2-CH_2-S-S-S-CH_2-CH_2-Cl and a pentasulfide formed by attaching two sulfur atoms to the middle sulfur of the trisulfide. Depending on conditions, even more sulfurs can be attached (as chains of sulfur hanging on to the middle sulfur). Very little disulfide is formed (Fuson et al. 1946a, 1946c). The proportions of polysulfides with various numbers of sulfurs, and of free sulfur, depend on formation temperatures and the age of the crude mixtures. The middle sulfur — and any sulfurs attached to it — would appear to be quite labile.

When HD was heated in a sealed tube at 180°C for 18 h, the products of reaction were 1,4-dithiane and 1,2-dichloroethane (Cl-CH_2-CH_2-Cl) in high yield (Bell et al. 1927). (1,4-Dithiane is a mustard impurity frequently found in groundwater near mustard disposal sites.) The reverse reaction, conversion of 1,4-dithiane plus excess 1,2-dichloroethane in a sealed tube at 180°C to mustard, was demonstrated by the same authors (though a small yield must be presumed). When HD was held at 137° to 145°C in an atmosphere of nitrogen, with 1,2-dichloroethane allowed to escape, some 1,4-dithiane was formed; the following compounds were also identified among the products (Fuson et al. 1946b):

Cl-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-Cl

1,2-Bis(2-chloroethylthio)ethane

and



Bis[2-(2-chloroethylthio)ethyl] sulfide

In addition, evidence existed that higher polymeric materials were present. With small amounts of water, HD (or H) would form some of the hydrolysis intermediates discussed in Section 3.5.1.

It has not been possible to find a listing for the composition of a "typical" sample of H; such an entity may not exist. It is instructive, however, to consider two old samples of H (probably Levinstein mustard) that were recently analyzed. In the first instance, a 75-mm projectile dating from the World War I era was discovered in Spring Valley, Washington, D.C.; it was subjected to proton NMR spectrometry and found to contain sulfur mustard of the composition (peak area of NMR spectrum down to 0.5%, with less abundant constituents not recorded here) shown in Table 5 (Brooks et al. 1994). Aside from HD, the main constituents correspond to Levinstein mustard impurities, products of thermal decomposition, and products of reaction with limited amounts of water described above.

Table 5. Composition of a World War I Sample of H from Spring Valley Analyzed in 1993 Down to 0.5%

Analyte	NMR Peak Area %
HD ($Cl-CH_2-CH_2-S-CH_2-CH_2-Cl$)	64.2
HD Disulfide ($Cl-CH_2-CH_2-S-S-CH_2-CH_2-Cl$)	11.8
1,4-Dithiane ($C_4H_8S_2$)	9.7
HD Trisulfide ($Cl-CH_2-CH_2-S-S-S-CH_2-CH_2-Cl$)	3.7
1,2-Bis(2-chloroethylthio)ethane ($Cl-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-Cl$)	3.7
1,2,3-Trithiolane ($C_2H_4S_3$)	1.4
1,4-Thioxane (C_4H_8OS)	1.1
1,2,5-Trithiepane ($C_4H_8S_3$)	0.9
1,2,3,4-Tetrathiane ($C_2H_4S_4$)	0.8
$Cl-CH_2-CH_2-S-CH_2-CH_2-O-CH_2-CH_2-Cl$	0.7

The second sample, from an old chemical munition of undisclosed origin, was analyzed in July 1993 by gas chromatography/mass spectrometry (GC/MS); peak areas were measured, as shown in Table 6 (Rohrbaugh 1994).

HD stored in a 1-ton container (No. HD-U-2296-CTF-N), probably dating to after World War II, was also sampled and analyzed in July 1993 by GC/MS. Results are shown in Table 7 (Rohrbaugh 1994).

Table 6. Composition of an Old Sample of H Analyzed in 1993

Analyte	GC/MS Peak Area %
HD ($Cl-CH_2-CH_2-S-CH_2-CH_2-Cl$)	62.2
HD Disulfide ($Cl-CH_2-CH_2-S-S-CH_2-CH_2-Cl$)	10.9
1,4-Dithiane ($C_4H_8S_2$)	3.2
HD Trisulfide ($Cl-CH_2-CH_2-S-S-S-CH_2-CH_2-Cl$)	9.6
1,2-Bis(2-chloroethylthio)ethane ($Cl-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-Cl$)	2.6
1,2,3-Trithiolane ($C_2H_4S_3$)	2.4
1,4-Thioxane (C_4H_8OS)	0.1
1,2,5-Trithiepane ($C_4H_8S_3$)	0.9
1,2,3,4-Tetrathiane ($C_2H_4S_4$)	1.4
$Cl-CH_2-CH_2-S-CH_2-CH_2-O-CH_2-CH_2-Cl$	0.4
1,2-Dichloroethane ($Cl-CH_2-CH_2-Cl$)	3.2
HD Tetrasulfide ($Cl-CH_2-CH_2-S-S-S-S-CH_2-CH_2-Cl$)	0.6
$Cl-CH_2-CH_2-S-CH_2-CH_2-CH_2-Cl$ or isomer	0.3
$Cl-CH_2-CH_2-S-CH_2-CH_2-CH_2-CH_2-Cl$ or isomers	0.8
$Cl-CH_2-CH_2-S-CH_2-CH_2-S-S-CH_2-CH_2-Cl$	0.2
Tetrachloroethene ($Cl_2C=CCl_2$)	0.3
Sulfur (S_8)	0.5

Table 7. Composition of a Sample of HD from a 1-Ton Container Analyzed in 1993

Analyte	GC/MS Peak Area %
HD ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$)	89.2
HD Disulfide ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$)	0.1
1,4-Dithiane ($C_4H_8S_2$)	1.2
1,2-Bis(2-chloroethylthio)ethane ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$)	4.7
1,2,5-Trithiepane ($C_4H_8S_3$)	0.1
1,2-Dichloroethane ($Cl\text{-}CH_2\text{-}CH_2\text{-}Cl$)	2.4
$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl$ or isomer	0.4
Four $Cl\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Cl$ isomers	1.7

To summarize, chemically impure mustard (H) behaves more or less like the distilled product (HD) but contains a much higher proportion of impurities and is likely to be more viscous than HD. The toxicity and environmental fate of most of the impurities have not been thoroughly characterized.

4.0 CONCEPTS OF CONTAMINATION AND REACTIVE DECONTAMINATION

The following subsections of this document often refer to interactions between agents and "substrates." The U.S. Army frequently tests the effects of chemical agents on various types of military equipment, followed by decontamination solutions and procedures to decontaminate the various materials tested. The materials tested are referred to as "substrates".

4.1 Exposure of Materials to Vapor-State and Liquid Agents

The exposure of impermeable, chemically unreactive substrates (such as stainless steel or glass) to HD, GB, GD, and VX in the vapor state will result in very little sorption of the agents. Aeration will lead to very rapid loss of any residual agent following decontamination. By contrast, painted metal is expected to absorb a small amount of agent vapors; plastics and elastomers would absorb more, depending to a considerable degree on the time of exposure preceding decontamination. For a detailed discussion of agent sorption/desorption in organic matrices, see Appendix C.

Exposure of substrates to liquid agents would permit higher loadings than exposure to vapors. A fairly volatile agent, such as GB, deposited on a nonporous unreactive surface, would evaporate quickly even without decontamination; whereas an agent of low vapor pressure, such as VX, would tend to persist. Permeable polymeric substrates would tend to absorb agents, especially those of low volatility, making the agents largely inaccessible to decontaminants. The longer the delay between application of agent to substrate and application of decontaminant (especially for agents of low volatility) the more deeply penetrating the agent would be.

4.2 Interactions between Agents-on-Substrates and Decontaminant Solutions

The solubility of an agent in a decontaminating solution strongly affects the ease of decontamination. Thus, GB, which is infinitely miscible with water, should be easily and rapidly removed from an impermeable surface such as stainless steel. H or HD, being relatively insoluble, might require lengthy contact with decontaminant solution to achieve decontamination of such a surface. If the agent has been absorbed by a permeable substrate, such as paint, time will be required for it to diffuse out to the decontaminant. Most active decontaminant ingredients do not penetrate the material to attack the agent within. From a practical point of view, the time of contact between permeable substrates and decontaminant solutions have to be prolonged to effect complete decontamination where the rate of reaction is limited by the rate of diffusion of the agent back out of the substrate.

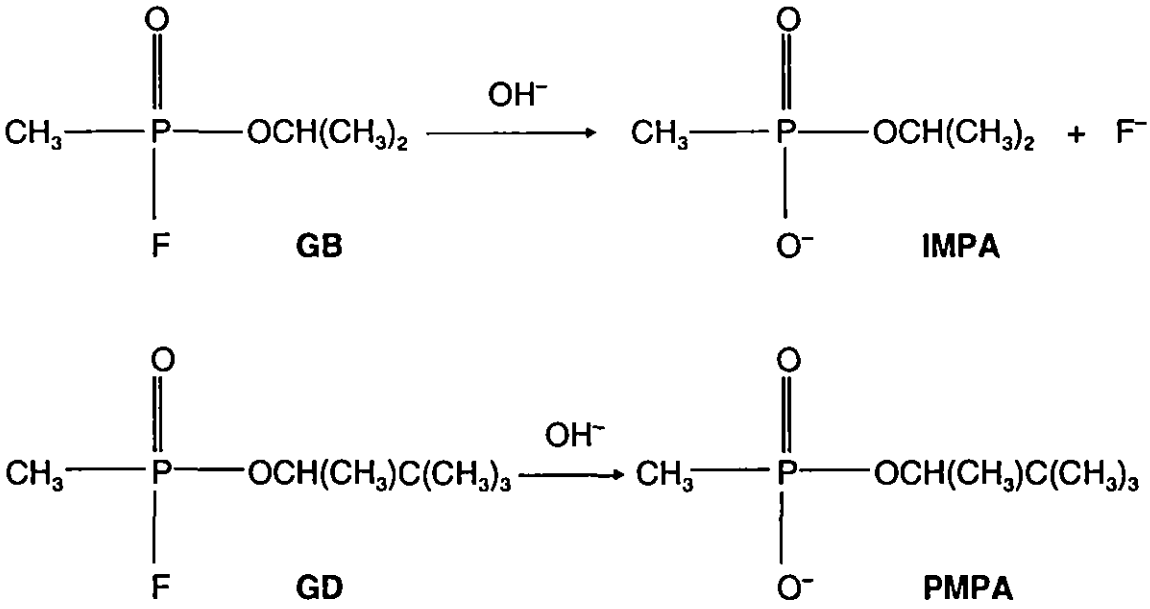
Once agent and reactive decontaminants have been brought together in the decontaminating solution, speed and efficacy of decontamination is controlled by the reaction rates (kinetics).

5.0 MAJOR REACTIVE SYSTEMS FOR DECONTAMINATION

5.1 Reactions with Aqueous or Aqueous-Alcoholic Alkaline Solutions

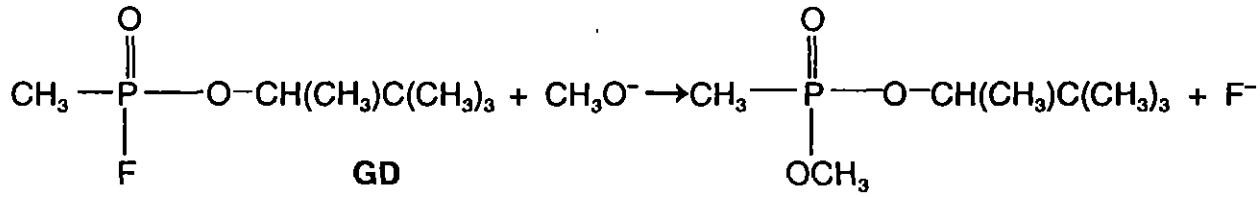
5.1.1 GB and GD

GB and GD are rapidly hydrolyzed by water at high pH through reaction with hydroxide ion:



As reported in Section 3.2, the half-life of GB at pH 10 (a reasonable pH for a sodium carbonate solution) is approximately 5 min; one may estimate the half-life for GD (see Section 3.3) at the same pH as 8.3 min (or, accepting the value from Yang et al. [1992], 12 min). Thus, in an hour, five or more half-lives would elapse, and

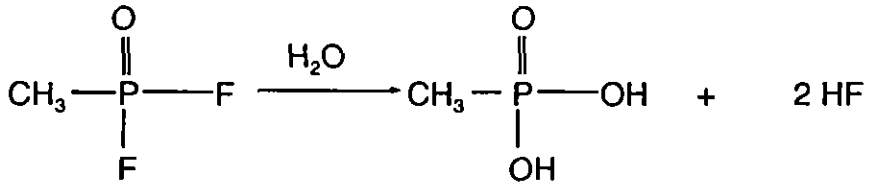
the concentration of agent would be no more than 3% of its original value. In 4 h at pH 10, the concentration of either of these agents would be less than one millionth of its original concentration. The reaction rate would be a thousandfold greater at pH 13 (the approximate pH of 0.4% sodium hydroxide) than at pH 10. Whereas GB is infinitely miscible with water, GD is soluble only to the extent of about 2%. The solubility of GD can be increased by using a solvent mixture consisting of a small proportion of water with a large proportion of methanol (or another alcohol); the alcohol does not appear to depress the reactivity of G-agents with sodium hydroxide in the solution to a significant degree. The decontaminating solution, in this case, contains not only hydroxide ion but also methoxide ion. Alcoholysis of GD by the latter occurs, to some degree, in parallel with the hydrolysis reaction depicted above, to form methyl pinacolyl methylphosphonate, an ester:



GD

This ester would eventually undergo hydrolysis to form pinacolyl methylphosphonic acid and perhaps some methyl methylphosphonic acid.

Methylphosphonic difluoride, a potential impurity of GB and GD, would rapidly hydrolyze to methylphosphonic acid (MPA) and its anions on exposure to water, especially at high pH.



MPA

Also present as impurities in the G-agents are dialkyl methylphosphonates such as DIMP. Such esters undergo relatively slow basic hydrolysis to salts of alkyl methylphosphonic acids. Alkyl methylphosphonic acids, which are also the phosphorus-containing hydrolysis products of GB or GD, are extremely resistant to basic hydrolysis, although they are slowly hydrolyzed in strong acid at elevated temperatures (Kingery and Allen 1994, 1995). These alkyl methylphosphonic acids can undergo catalyzed hydrolysis, biologically or in the presence of reactive soils, to form methylphosphonic acid (Kingery and Allen 1994, 1995). Kingery and Allen also showed that the latter is chemically quite stable although subject to slow biodegradation. Aqueous methylphosphonic and alkyl methylphosphonic acids can be routinely analyzed in water down to a level of 0.5 μg/L by ion chromatography (Kingery and Allen 1993).

To sum up, alkaline aqueous or alcoholic solutions rapidly hydrolyze GB and GD; the presence of an alcohol enhances the solubility of GD.

The diisopropyl carbodiimide added as a stabilizer for weapons-grade GB would be converted completely to N,N'-diisopropylurea by the strongly basic aqueous decontaminant (see Appendix B). The tributylamine stabilizer is unreactive towards base.

5.1.2 VX

The hydrolytic reactions of VX are complex and involve multiple pathways. Rates and products depend on pH (Epstein et al. 1974; Yang et al. 1990, 1992, 1993a, 1994; Szafraniec et al. 1993), temperature and VX concentration (Yang et al. 1994). VX is not subject to acid-catalyzed hydrolysis but does undergo water- and hydroxyl ion–catalyzed hydrolysis. The major products under most conditions are those of P-S cleavage, giving ethyl methylphosphonic acid and DESH. DESH, especially under alkaline conditions, is easily oxidized by oxygen to form EA 4196.

Contrary to the report by Epstein et al. (1974) that P-S cleavage is the only reaction at pH >10, it now appears that formation of the products of ethoxy (i.e., C-O) cleavage, namely ethanol and EA 2192, is significant at both neutral and alkaline pH. Thus, at 22°C, Yang et al. (1992, 1993a) report a 13% yield of EA 2192 from 0.01 M VX in aqueous 0.1 M sodium hydroxide; at 23°C, Szafraniec et al. (1993) report the following molar sodium hydroxide concentrations and EA 2192 yields: 0.25, 11%; 1.25, 16%; and 2.0, 17%. Further, Yang et al. (1990) report a 22% yield of EA 2192 for 0.05 M VX in 2 M sodium hydroxide dissolved in water containing 10% by volume of 2-propanol (to solubilize the VX). It is important to recognize that the still quite toxic EA 2192 is quite resistant to hydrolysis, as will be seen below.

A third set of hydrolysis products was reported for the neutral pH range, namely those arising through nitrogen-assisted C-S cleavage and producing as the major (but probably not only) products, diisopropylaminoethyl sulfide and O-ethyl methylphosphonothioic acid (Epstein et al. 1974; Yang et al. 1990).

While the C-O cleavage products have been seen under very alkaline conditions in strictly aqueous solution, studies with the simulant O,S-diethyl methylphosphonothioate have indicated that presence of a preponderance of an alcoholic solvent along with the alkali favors P-S cleavage. Thus, it is inferred that VX could be rapidly decontaminated by such strongly basic (e.g., with 0.15 M added NaOH) methyl or propyl alcoholic solutions without forming the product EA 2192. This holds true even when as much as 10% of water by volume is present. The enhanced and selective reactivity of VX in such solutions is a result of the high nucleophilic reactivity of the alkoxides formed by reaction between the alcohols and the added hydroxide ion; the effect is not due to decreased solvent polarity (Yang et al. 1993b). From these results with the simulant, it is predicted that, following reaction with VX, such alcoholic decontamination fluids would be free of EA 2192.

Concern for the presence of EA 2192 and EA 4196 stems from reports of their toxicity. EA 2192 is nearly as toxic as VX by the intravenous route, although considerably less so by the oral route, and is apparently not absorbed through the skin; its extremely low vapor pressure precludes it from being hazardous by inhalation (Durst et al. 1988). EA 4196 is believed to be a powerful vesicant, comparable in that respect to mustard gas (Small 1983).

The half-lives for disappearance of VX at 25°C in aqueous solution have been reported by Epstein et al. (1974) as shown in Table 8 (some of the values were actually determined for the diethylamino analog of VX that has virtually identical hydrolytic behavior). Durst et al. (1988) cited a reported half-life at pH 14 of 1.3 min (0.022 h, no temperature given).

For 22°C and 0.1 M aqueous sodium hydroxide, Yang et al. (1993a) reported a half-life for VX of 31 min (0.517 h). At the same temperature, with 10 times the concentration of sodium hydroxide, the half-life of EA 2192 was 7.4 days (178 h).

Under very alkaline conditions, the half-life of VX (in minutes) can be expressed (Szafraniec et al. 1993) as:

$$t_{½} = 2.17/([OH^-]^{1.2})$$

The half-life for EA 2192 can be expressed (in minutes) as:

$$t_{½} = 835/([OH^-]^{1.6})$$

Table 8. Hydrolysis Half-Lives for VX

pH		Half-Life (hours), 25°C
2.0		2,520
4.0		2,257
6.0		2,381
7.0		996
8.0		184
9.0		63
10.0		40.5
11.0		15
12.0	(approximately 0.01 M NaOH)	2.5
12.65		0.525
12.9		0.279
13.5		0.0529

Source: Epstein et al. (1974)

Because VX is a base, the pH resulting from its dissolution in water is sufficient to initiate its own hydrolysis. However, the acid generated by that reaction would gradually lower the pH, so that the apparent half-life would decrease with time. Yang et al. (1990) estimate 80 h as the "half-life for the spontaneous hydrolysis" of VX at 20°C. Szafraniec et al. (1990) made a 0.5% solution of VX in unbuffered water; the initial pH was 9.0, and this dropped to 7.5 in the course of hydrolysis. The overall first-order rate constant was 0.0121 h^{-1}1, so that the half-life was 57 h. Cleavage fractions are P-O, 0.54 (product EA 2192); P-S, 0.36; and S-C, 0.10. Thus, cleavage to produce EA 2192 was dominant under these conditions.

As can be seen in Section 3.4, the hydrolysis rate for VX at pH 10 and 25°C is about 375 times slower than for GB, and this holds more or less true at higher pH levels. Moreover, ordinary alkaline aqueous hydrolysis sufficient to destroy all the VX would not completely eliminate the toxicity (because of EA 2192). One hydrolysis product of VX,

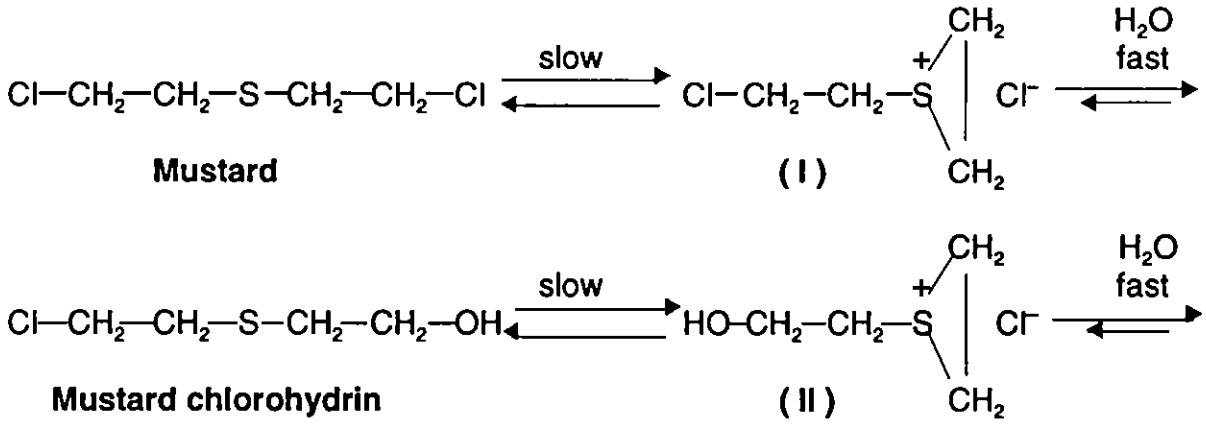
ethyl methylphosphonic acid (EMPA), has an environmental fate very similar to that of other alkyl methylphosphonates (see Section 5.1.1).

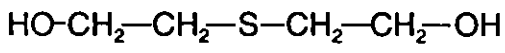
In sum, the hydrolysis chemistry of VX is complex. Hydrolysis is fastest under basic conditions and is enhanced by the presence of alcohols, which help to avoid formation of the undesirable EA 2192. Water-containing decontaminants convert the VX stabilizing agents, diisopropyl carbodiimide and dicyclohexyl carbodiimide, to N,N'-diisopropylurea and N,N'-dicyclohexylurea, respectively.

5.1.3 H and HD

H is a mixture of HD with various impurities in differing proportions that depend on the history of the particular lot. (Old samples of "HD" may contain some of those same impurities.) Because it is impractical to characterize the chemistry of H separately, most studies have involved fairly pure HD. For this reason, emphasis is placed on HD; this report also contains a few qualitative comments (based on best professional judgment) as to the chemical behavior and possible effects of the impurities.

For hydrolysis of HD with predominantly aqueous solutions, the two central facts are (1) dissolution of HD in water is extremely slow, though it can be facilitated by vigorous stirring, and (2) the rate of basic hydrolysis (via the intermediate 2-chloroethyl-2'-hydroxyethyl sulfide or "mustard chlorohydrin") to the predominant product, thiodiglycol, is not affected by the base concentration. The reason for the insensitivity to base concentration is that the formation of the cyclic sulfonium intermediates (I and II) is slow and rate-controlling, and it depends mainly on the nature of the solvent (Rosenblatt et al. 1975). The following reactions are observed almost exclusively when the ratio of water to HD is relatively high:

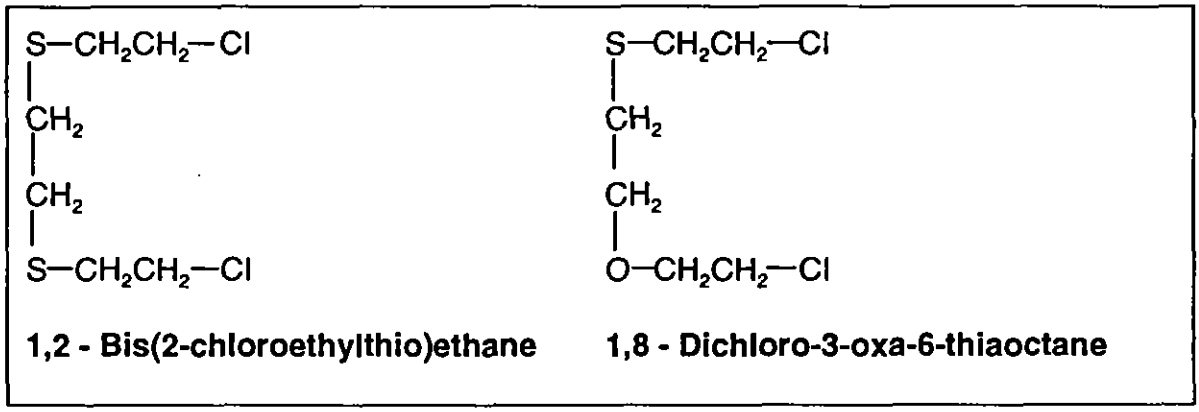




Thiodiglycol

Note that the hydrolysis of mustard chlorohydrin is somewhat faster than that of mustard, so that the chlorohydrin does not tend to accumulate in high concentration. If chloride ion is present, as it is in seawater, for example, the reaction is retarded because chloride ion reacts with the cyclic sulfonium intermediates I and II to reform HD. Strong nucleophiles, (e.g., thiosulfate) also react with the intermediates, competing with water or hydroxide for I and II, so that less thiodiglycol is formed (Ogston et al. 1948).

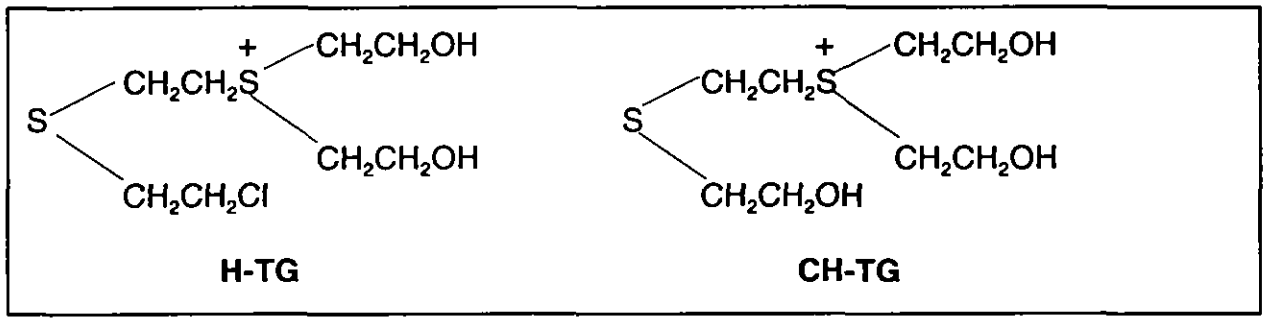
The impurities found in H, such as the polysulfides, might be expected to hinder the already slow dissolution of the agent, and, if they dissolved in water, to react more slowly with water than HD (or not at all). One impurity, 1,2-bis(2-chloroethylthio)ethane, is about five times as vesicant as HD itself; others, such as 1,8-dichloro-3-oxa-6-thiaoctane, are probably about as toxic as HD. Yet others, including the HD polysulfides, are considerably less vesicant; thus, the disulfide, Cl-CH_2CH_2-S-S - CH_2CH_2-Cl is reportedly 1/50 as vesicant as HD, and the trisulfide, Cl-CH_2CH_2-S-S-S-CH_2CH_2-Cl is not vesicant at all (Kinnear and Harley-Mason 1943).



Organic solvents that might be added to water to solubilize HD, so as to facilitate its hydrolysis, often significantly decrease the rates of formation of the sulfonium intermediates (Yang et al. 1986). When a relatively small amount of acetone (5%) was used to introduce a sample of mustard into water at 25°C, the rate constant for disappearance of HD was 0.00129 s^{-1} (Yang et al. 1986, citing Bartlett and Swain (1949)). This indicates a half-life of 0.693/(0.00129 x 60) = 9.0 min. The half-life would be somewhat less in pure water. In short, the concentration of HD could be reduced by a factor of 1 million in 3 h, provided dissolution in water could be effected with the addition of only a very small amount of a suitable solvent. (Note that Bartlett and Swain [1949] reported the initial rate constant for disappearance of HD as 0.002585^{-1}).

Although the hydrolysis reaction occurs rapidly, it seems that a tendency exists in quiescent conditions for HD to polymerize at the HD/water interface, which interferes with transfer of HD to the aqueous solution and thus shields the bulk agent from hydrolysis reactions (MacNaughton and Brewer 1994). The Committee on Alternative Demilitarization Technologies (1993) states: "The chemical problem is that the intermediate products are cyclic or oligomeric sulfonium salts, which are relatively unreactive and which moreover have the potential for slowly reforming mustard." Yang et al. (1987) write that "the enduring toxicity of mustard gas in the environment can hardly be explained unless additional transformations of mustard gas into stable products of similar toxicity exist." They note the toxic effects of H-2TG (see structure in Section 3.5.1) and the less stable H-TG to bolster this argument. As evidence, one may cite an experiment that sought oligomeric sulfonium salts under conditions in which a limited amount of water was in contact with HD for a moderately long period. Equal volumes of HD and water (as a two-phase system) were allowed to stand; after two months at least 50% of the original HD phase was

still present. NMR spectrometry indicated that the aqueous phase contained a preponderance of the H-2TG dication, a small amount of thiodiglycol, and a smaller amount of CH-TG cation (Yang et al. 1987).



A somewhat different picture is presented by the analysis of products of bulk decontamination of mustard stocks. After 1,000-gallon batches of H stored by the Canadian government were each hydrolyzed with 5,000 pounds of calcium hydroxide and 2,500 gallons of water at 100°C, they were allowed to stand for several years. Each batch separated into two layers: a colorless to pale yellow fluid and a paste-like yellow-brown sludge. The liquid layers contained five nonionic species (no analytical methods were applied to detect anions such as H-2TG or CH-TG) (Table 9) (D'Agostino and Provost 1985). The sludge contained a large number of sulfur compounds (at least 25 compounds), but most could not be identified; those that were characterized are listed in Table 10. The fact that such compounds survived may indicate that they are less reactive than HD itself. Because cations such as H-2TG, CH-TG, and H-TG could not have been identified by the methods employed, one should not conclude that these toxic entities were absent.

It is not clear how high the ratio of water to HD would have to be to ensure that toxic cations (such as H-2TG, H-TG, CH-TG, or others not yet identified) would be eliminated by hydrolysis and that HD could not form again. It is likely, however, that use of alkaline aqueous solutions under conditions of decontamination, where the aqueous decontaminant is in large excess, would completely transform HD to essentially nonhazardous products, provided contact times were sufficiently long (e.g., hours).

Table 9. Organic Solutes in the Liquid Phase Present in Calcium Hydroxide Hydrolysates of H (Mustard Gas)

Thiodiglycol ($C_4H_{10}O_2S$)
1,4-Oxathiane (C_4H_8OS)
(2-Vinylthio)ethanol (C_4H_8OS)
1,4-Dithiane ($C_4H_8S_2$)
Mustard Chlorohydrin (C_4H_9ClOS)

Table 10. Organic Solutes Identified in the Chloroform Extracts of the Calcium Hydroxide Sludge Hydrolysates of H (Mustard Gas)

1,4-Oxathiane (C_4H_8OS)
(2-Vinylthio)ethanol (C_4H_8OS)
1,4-Dithiane ($C_4H_8S_2$)
HD Disulfide ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$)
HD Trisulfide ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}S\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$)
1,2,5-Trithiepane ($C_4H_8S_3$)
2-Methyl-1,3-oxathiolane (C_4H_8OS)
5-Oxa-1,2-dithiepane ($C_4H_8OS_2$)

5.2 Reactions with Aqueous Hypochlorite Solutions

Hypochlorite solutions (commonly known as bleach) are efficacious decontaminants but are corrosive (Hovanec et al. 1993). Although they meet the requirements of detoxifying an exposed material, the utility of the material may be sacrificed.

5.2.1 GB and GD

Commercial aqueous sodium hypochlorite solutions, as well as solutions or suspensions containing calcium hypochlorite, are somewhat alkaline, so that G-agents would be hydrolyzed fairly rapidly in such solutions even without the effects of hypochlorite ion (see Section 5.1.1).

Epstein et al. (1956) studied the strong catalytic effect of aqueous hypochlorite ion on the hydrolysis of GB. They determined the second order rate constant to be 600 M^{-1} min^{-1} at 25°C and cited a K_a value of 4×10^{-8} for hypochlorous acid (HOCl). If one assumes a sodium hypochlorite (MW = 75.5) concentration of 3% in a commercial bleach sample and a pH of 8, the observed first-order rate constant (k_{obs}) for hypochlorite-catalyzed hydrolysis of GB is calculated to be:

$$(0.03 \times 1000/75.5) \times (4 \times 10^{-8}/[1 \times 10^{-8} + 4 \times 10^{-8}]) \times 600 \quad = \quad 191\ min^{-1}$$

The half-life would be 0.693/191 = 0.00363 min, or 0.218 s. Thus, the concentration would decrease more than a millionfold in less than 5 s. As the pH decreases, the concentration of hypochlorite ion decreases and that of HOCl increases. The latter has no effect on GB hydrolysis, so decreases in pH to levels below 8 decrease the decontaminant's effectiveness. Although no analogous study has been conducted with GD, the rate constants observed with hypochlorite ion are not expected to be appreciably lower than those for GB.

Therefore, strong commercial bleach, which contains sodium hypochlorite, and slurries of solid bleaches that contain calcium hypochlorite are very effective in catalyzing the hydrolysis of GB (above) and GD (Eskanow 1978).

Hypochlorite solutions that have stood for any length of time contain chlorate ion as a contaminant because of the following disproportionation reaction (Bodek et al. 1988):

$$2\ HOCl + OCl^- \rightleftarrows ClO_3^- + 2\ H^+ + 2\ Cl^-$$

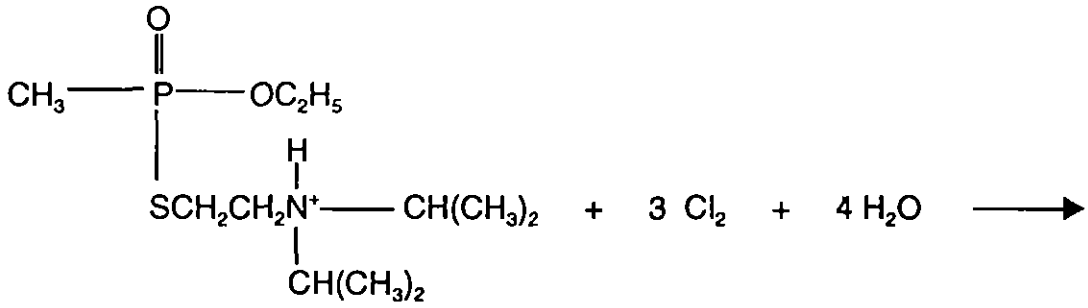
Chlorate ion should not be overlooked as a possible toxicant.

5.2.2 VX

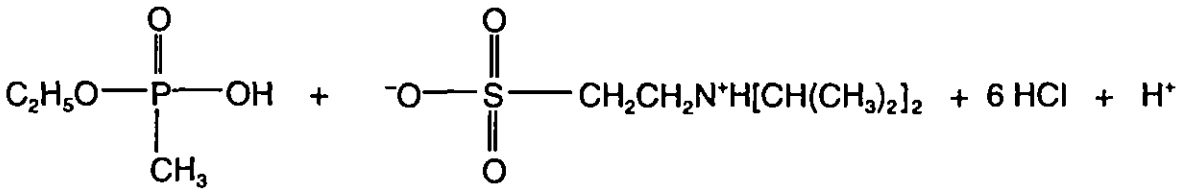
Aqueous hypochlorite solutions react differently with VX at low (acidic) pH than at high (alkaline) pH. At low pH, VX is protonated on the nitrogen (which greatly enhances the agent's water solubility), and is thus protected at that site (Yang et al. 1992). Also, if the acidic (proton-rich) medium contains chloride ion, the very reactive oxidizing species elemental chlorine (Cl_2) must be present, that is:

$$HOCl + H^+ + Cl^- \rightleftarrows Cl_2 + H_2O.$$

Under these circumstances, the reaction is:



Protonated VX

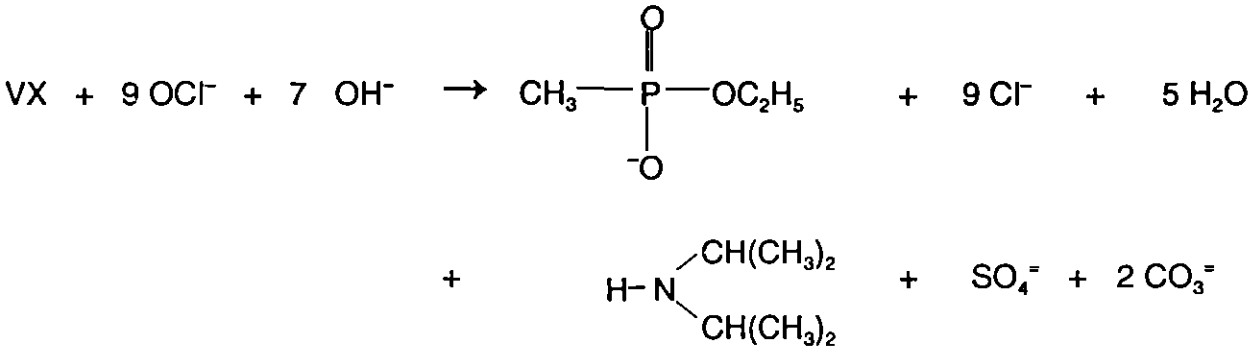


Ethyl methylphosphonic acid
EMPA

Diisopropyltaurine

The reaction with gaseous chlorine would probably be useful to destroy VX only on a large scale because facilities would be needed to prevent release of chlorine fumes and to avoid the corrosive effects of that element. In the procedure conducted at Tooele Army Depot (Durst et al. 1988), 100-pound batches of VX were dissolved in 1.5 N hydrochloric acid (1:3 v/v) and chlorine gas was added (rather than HOCl, as discussed above) until the solution maintained the green color of chlorine. The reaction was rapid and strongly exothermic. The destruction efficiency was determined to be 99.999999%. Among the products found was N,N'-dicyclohexylurea, which was formed from dicyclohexyl carbodiimide, the VX stabilizer mentioned earlier. Even if only HOCl (and not Cl_2) is present, the oxidation can proceed in a similar fashion (Yang et al. 1992).

On the moderately basic side, because the unprotonated VX nitrogen is available, initial oxidative attack by HOCl (more likely than OCl^-) probably occurs preferentially as an electrophilic oxidative attack on the nitrogen. This is logical, because the nitrogen is electron-rich. Unlike other oxidants whose reactions with VX and model compounds have been examined (Yang et al. 1990), however, the chlorine system (specifically $HOCl/OCl^-/Cl_2$) is so complex that the mechanisms involved in chlorinolysis of VX in basic solution have not yet been defined. With sufficient excess hypochlorite, the stoichiometry of the reaction has been reported (Durst et al. 1988) as:



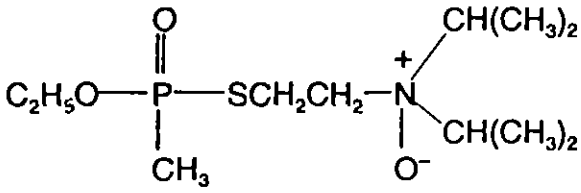
Diisopropylamine

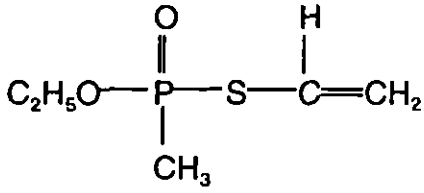
The reaction was characterized by Durst et al. (1988) as rapid (half-life = 1.5 min at pH 10), having been used for demilitarization of VX. However, it is considered less effective than acid chlorinolysis. The nature of the products is pH-dependent.

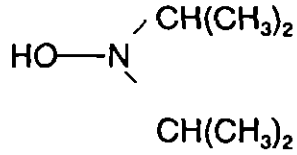
With reaction occurring very rapidly in basic chlorinolysis and perhaps in branching sequences, the potential intermediates are numerous, but most might not be stable enough to permit their isolation. Table 11 depicts some intermediates suggested by Yang et al. (1990) with other oxidants. These compounds, about which almost nothing is known, are not likely to explain the formation of diisopropylamine; it would more reasonably have been formed via an N-chlorammonium intermediate in a kind of oxidative fragmentation reaction (Dennis et al. 1967).

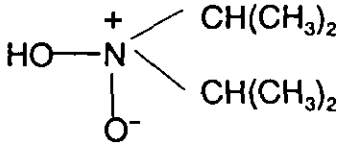
It may be concluded that, under appropriate conditions, the diisopropylaminoethylthio moiety of VX can be efficiently and permanently disrupted by chlorinolysis; thus, the VX is completely destroyed. These conditions need to be more precisely defined.

Table 11. Possible Intermediates in the Chlorinolysis of VX









5.2.3 H and HD

The sulfur moiety of HD is readily subject to oxidation. Various forms of hypochlorite-containing materials have been used to effect oxidative reactions, including bleach solution (approximately 3-5% aqueous sodium hypochlorite, available on grocery shelves); chlorinated lime [approximately Ca(Cl)(OCl)]; and "high test hypochlorite" [HTH, with the formula $Ca(OCl)_2$]. When solid chlorinated lime or HTH are used, reaction with HD may be violently exothermic; with the hypochlorite source in aqueous slurry, reaction is more easily controlled. While the reaction pathway varies with the proportion of reactants and temperature, the mineralization of HD is essentially complete in the presence of a sufficient excess of hypochlorite (Durst et al. 1988):

$$(Cl\text{-}CH_2\text{-}CH_2)_2S + 14\ OCl^- \rightarrow SO_4^{=} + 16\ Cl^- + 4\ CO_2 + 4\ H^+ + 2\ H_2O$$

HD

Durst et al. (1988) cite an Edgewood Arsenal internal memorandum:

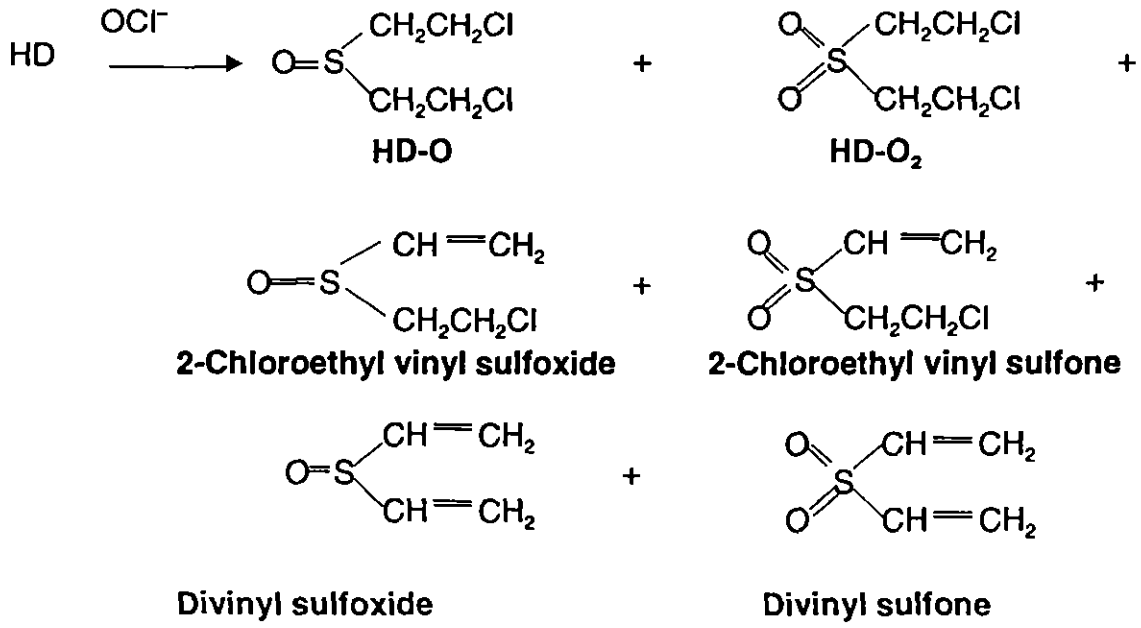
> In actual decontamination of HD with calcium hypochlorite, scaled-down amounts, corresponding to ratios of 11.7 lb of HD to 100 lb of HTH in 108 gal of water, were stored for several days at an ambient temperature, treated with sodium thiosulfate to remove excess hypochlorite, and extracted with hexane. The extracts were submitted to GLC [gas-liquid chromatography] with sensitivity of 1 ppm [part per million] of HD in hexane and results indicated essentially complete decontamination.

[Note that a ratio of 19 OCl^-:1 HD was employed here, rather than the minimal 14:1 ratio required by the equation.]

Citing Yurow (1981), MacNaughton and Brewer (1994) point out that, "Theoretically, HD can be completely decomposed to sulfate, chloride and carbon dioxide; however, due to the low solubility of HD in aqueous solutions, poor mixing, or non-stoichiometric proportions, other products such as the sulfoxide or sulfone [see discussion below] are produced." MacNaughton and Brewer go on to say that the reaction of HD is pH-dependent. Reactions in alkaline media "are primarily oxidative, while in acid and neutral solutions, chlorination takes place."

Yang et al. (1992) have also illuminated the subject with a number of observations, as well as a scheme showing some of the early reaction products:

> The reactions of chemical agents are so vigorous that ... agents can be converted to less or nontoxic products at the liquid-liquid (bleach solution) or liquid-solid (bleach powder) interface in a few minutes. Solubilization of the agents in the same medium as the bleach is not required. As shown in [the scheme below], HD is converted into a series of oxidation and elimination products. It is believed that the sulfoxide (HD-O) is formed first, followed by sulfone ($HD-O_2$) formation. Subsequently, both oxidation products undergo elimination reactions in the strongly basic solution to produce the corresponding monovinyl and divinyl sulfoxides and sulfones, although small amounts of additional products are also present in the final solution.



According to Yang et al. (1992), the observed rates of oxidation by anionic oxidants (such as OCl^-) decrease as the polarity of the solvent decreases.

As shown above, information regarding the initial products of mustard oxidation is available; this comes from studies at low hypochlorite-to-mustard ratios, in dilute solution, at short times, or under other circumstances that permit isolation of somewhat reactive and unstable intermediates. When the reaction is pushed to the ultimate, complete mineralization can apparently occur. Evidently researchers have not been successful in tracking the fate of identified products such as divinyl sulfone in the presence of hypochlorite, as these products are converted to sulfate, carbon dioxide, and water. In part, this reflects the instability of the intermediates. But it may also reflect the diversity of roles that various chlorine species may play. Depending on pH and on the concentrations of the species involved, the following oxidative chlorine species might be in equilibrium with OCl^- (i.e., hypochlorite ion) (Rosenblatt 1975): Cl_2, Cl_3^-, HOCl, Cl_2O, and H_2OCl^+. Each may have its own spectrum of reactivity; for example, hypochlorite is a very potent nucleophile as compared to its basicity towards protons, and so one would expect it to attack sulfonium salts like the cyclic sulfonium salt, H-2TG and H-TG, as described in Section 5.1.3. Moreover, some of the reactive uncharged chlorine-containing species (perhaps the less polar ones) may have the ability to cross the aqueous-organic boundary, diffuse, and react with material in the organic phase. To gain insight into such behavior would require developing appropriate hypotheses and designing experiments to test them.

If little is known about mechanisms of reaction of HD with chlorine species, even less is known about reactions of the sulfur-containing impurities of H. Under conditions favoring the mineralization of HD, it is quite probable that the extra, and rather labile, sulfurs of mustard polysulfides would be easily oxidized to sulfate. Other sulfur-containing impurities, too, would probably be oxidized — if not to sulfate, then at least to relatively harmless sulfoxides, sulfones, or sulfonic acids. With decreasing ratios of hypochlorite to oxidizable sulfur and carbon, the possibility that some toxic species could escape destruction would increase. Nevertheless, given enough contact time, under the usual decontamination conditions, it is likely that H would be completely detoxified — no less so than HD.

In summary, given sufficient contact, hypochlorite solutions are excellent decontaminants for H and HD.

5.3 Significance of Residual Products

Decontamination solutions are by nature reactive and must be used in excess to ensure complete removal of the highly toxic substances against which they are used. To avoid the possibility of adverse effects on the environment or on potential human receptors, those excess amounts should always be neutralized following their employment; neutralization should be an integral part of the overall decontamination process. Unfortunately, among the residues from decontamination with bleach, chlorate ion is apt to be found (see Section 5.2.1); this ion is not readily destroyed by neutralizing agents (such as sulfite ion) that react so easily with hypochlorite.

Fluoride ion, an inorganic product of GB and GD hydrolysis, is both an essential nutrient and, at higher levels, somewhat toxic. The organic products of basic or hypochlorite-catalyzed hydrolysis of GB and GD, as well as one of the products of VX hydrolysis, are alkyl methylphosphonic acids, essentially harmless, though under certain conditions they could form toxic (cholinesterase inhibiting) anhydrides. These alkyl methylphosphonic acids are degraded through catalysis by metals in the soil and by soil organisms, at site-specific rates, to methylphosphonic acid; this, like its precursors, is essentially harmless. Degradation of methylphosphonic acid to inorganic phosphate occurs only microbially and at a much slower rate (Kingery and Allen 1994).

Some of the products of VX hydrolysis are considered quite toxic, which is why alkaline alcoholysis or treatment with hypochlorite is preferred for decontamination.

The products of mustard hydrolysis are harmless when water is present in large enough excess and contact with the aqueous decontaminant is sufficiently prolonged. At lower ratios of water to H or HD, toxic intermediates would be of concern.

Alkaline chlorinolysis of VX with sufficient hypochlorite produces two organic products of relatively low toxicity, diisopropylamine and the alkyl methylphosphonic acid. At low pH, the latter is also formed, along with diisopropyltaurine (2-diisopropylaminoethanesulfonic acid), through the action of Cl_2.

Alkaline chlorinolysis of H or HD with sufficient hypochlorite causes complete mineralization and is generally considered a much more rapid process than hydrolysis.

Contact with water would cause hydrolysis of the additive N,N'-diisopropylcarbodiimide to N,N'-diisopropylurea and of the additive N,N'-dicyclohexylcarbodiimide to N,N'-dicyclohexylurea. Under conditions of chlorinolysis, these ureas could become N,N'-dichlorinated. (Direct degradation of the carbodiimides by chlorine-containing oxidants to still other products is a possibility, but no information has been found on the subject.) The N,N'-dichlorinated compounds would be reduced back to the corresponding ureas during neutralization.

Tributylamine, sometimes an additive for GB, would not be affected by hydrolysis. It would probably be oxidatively dealkylated to dibutylamine and butyraldehyde by hypochlorite (Rosenblatt and Burrows 1982).

It may be concluded that, depending on the exact conditions, chemical decontamination of the agents of concern can form a variety of residual products.

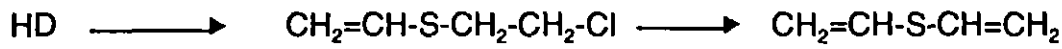
6.0 ALTERNATIVE LIQUID DECONTAMINATION SYSTEMS

The variety of possible decontaminants — other than the principal systems discussed above — that could be used to decontaminate various types of substrate materials is large; not all could be addressed in this review, but examples of those types applicable to equipment decontamination systems are presented below.

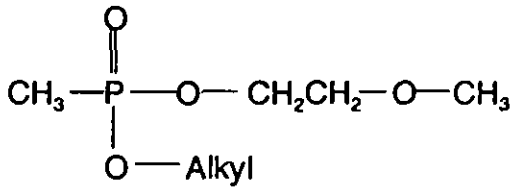
6.1 DS-2

Decontamination Solution 2 (DS-2) is a polar, nonaqueous, nonoxidizing liquid composed of 70% diethylenetriamine, 28% 2-methoxyethanol, and 2% sodium hydroxide by weight. It is a general-purpose, ready-to-use, reactive decontaminant with long-term storage stability and a large operating temperature range (-26° to 52°C). With this mixture, the half-lives for GB, VX, and HD were found to be <30 s, <7 s, and 2.3 s, respectively, at ambient temperature. Unfortunately, because of the low content of sodium hydroxide, DS-2 is subject to rapid depletion, and relatively large volumes must be used to ensure effective decontamination of appreciable quantities of agents. Moreover, it is corrosive to the skin, eyes, and lungs, as well as to paint, plastics, rubber, leather, and wood (Durst et al. 1988; Yang et al. 1992). Moreover, DS-2 is combustible. To minimize corrosion problems, the decontamination contact time of DS-2 with most painted surfaces is limited to 30 min, followed by a water rinse (Yang et al. 1992).

The reactive component of DS-2 is the strong nucleophile (or "superbase") CH_3-O-CH_2-CH_2-O^-, whose activity is probably enhanced because the counterion, Na^+, is complexed by the diethylenetriamine component (Durst et al. 1988; Yang et al. 1992). The main or only product of DS-2 with HD is divinyl sulfide, formed through consecutive elimination reactions (Durst et al. 1988; Yang et al. 1992):

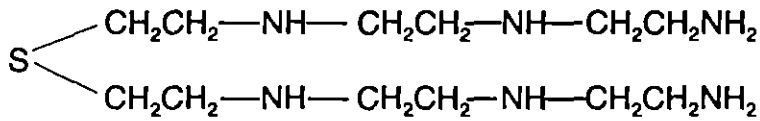


With G-agents and VX, fluoride or diisopropylaminoethylthio groups (respectively) are initially displaced by CH_3-O-CH_2-CH_2-O^- to give



In time, these diesters further decompose to other esters or part-ester anions that are essentially nontoxic (Yang et al. 1992).

Exposure to air or relatively large amounts of water decreases the efficacy of DS-2. Carbon dioxide is absorbed from the air to form carbonate salts that increase the solution's viscosity, and water causes reversion of CH_3-O-CH_2-CH_2-O^- to CH_3-O-CH_2-CH_2-OH. In the case of HD, depletion of CH_3-O-CH_2-CH_2-O^- prevents the consecutive elimination reactions shown above; instead, substitution with diethylenetriamine occurs to form, more slowly, amine derivatives such as



(Yang et al. 1992).

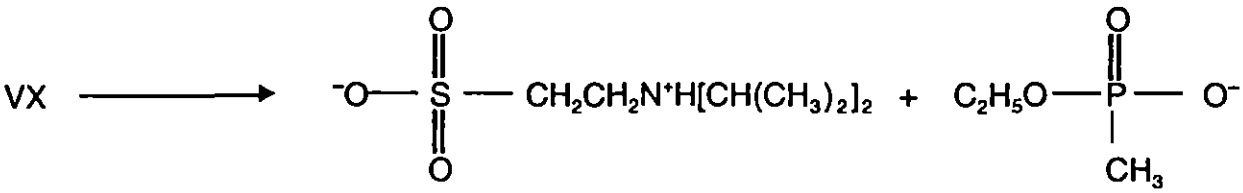
Basic formulations related to DS-2 include 70% methyl cellosolve/30% of a 50% aqueous sodium hydroxide solution and monoethanolamine. Both are effective against HD. Monoethanolamine, in particular, has the advantage of a high flash point, low toxicity, low cost, stability, and lack of corrosivity to metals (Durst et al. 1988). When combined with 4-N,N-dimethylaminopyridine (sometimes described as a "supernucleophile"), monoethanolamine has been employed for destruction of GB (Durst et al. 1988).

In summary, DS-2 and related materials can be quite effective but are costly and sometimes corrosive decontaminants.

6.2 Oxidizing Systems

6.2.1 Alkaline Hydrogen Peroxide and Peroxy Acids

Whereas a significant fraction (13%) of an 0.01 M solution of VX in 0.1 M sodium hydroxide is converted to the toxic EA 2192 (see Sections 3.4 and 5.1.2), adding 1% hydrogen peroxide is sufficient to preclude formation of any EA 2192, with mainly the following transformation occurring:



Diisopropyltaurine **EMPA**

The reaction is also considerably faster in the presence of 1% hydrogen peroxide (half-life for VX disappearance = 42 s at 22°C, as opposed to 1,860 s in the absence of the peroxide). Because this effect is due to initial nucleophilic attack on phosphorus by the anion of hydrogen peroxide ($pK_a = 11.8$), it only occurs at high pH and not in neutral solution. (Note that in a basic aqueous medium the solubility of VX is poor [Hovanec et al. 1993].) The reaction between EA 2192 and hydrogen peroxide under these conditions is much slower (Yang et al. 1993a). G-agents would be rapidly hydrolyzed not only because of catalysis by the hydroperoxide anion (Larsson, 1958) but simply because of the high pH.

Oxone is a commercial mixture, 2 $KHSO_5$ - K_2SO_4 - $KHSO_4$, the solution of which has a pH of 2.3 at 20°C. Oxidation of VX by Oxone formed N,N-diisopropylaminoethanesulfonic acid (diisopropyltaurine) and ethyl methylphosphonic acid almost exclusively. With a 0.01 M solution of this oxidant and 5 x 10^{-4} M VX, the observed half-life for VX was 19 min. At the low pH (high acidity) of the reaction mixture, VX dissolved readily and the nitrogen was shielded, through protonation, from oxidation to the N-oxide or products thereof (Yang et al. 1990). EA 2192 was not formed at all, which might be expected because the initial oxidation of the sulfur made the P-S bond extremely vulnerable to hydrolytic cleavage. Because of the high effectiveness of Oxone towards VX, this oxidant was tested against HD. In a solution of 0.05 M HD, 0.1 M Oxone, and 15 vol % N-methyl-2-pyrrolidone (added to help dissolve the HD), HD was oxidized immediately to the sulfoxide (see Section 5.2.3), which converted within an hour to the sulfone (Yang et al. 1992). Hovanec et al. (1993) have observed that N-methyl-2-pyrrolidone at a level of <20% does little to improve the solubility of HD and that it causes the Oxone to decompose. Oxone does not oxidize G-agents, but it is acidic enough to catalyze their slow hydrolysis (Yang et al. 1992).

Like Oxone, certain other peroxygen-containing oxidants are effective against HD and VX, notably *m*-chloroperoxybenzoic acid and magnesium monoperoxyphthalate (Yang et al. 1992). It should be pointed out that organic peroxides tend to be dangerously unstable.

6.2.2 Aqueous Fichlor

Fichlor (sodium N,N'-dichloroisocyanurate monohydrate) is quite stable in water, as compared to calcium hypochlorite, though its stability is pH-dependent. It has been used for laboratory-scale decontamination of VX (Durst et al. 1988). The products with VX are EMPA and diisopropyltaurine (Yang et al. 1992). Durst et al. (1988) record that Fichlor "was reported for destruction of HD, GD, and VX on paint surfaces and the test results were compared to those for other decontaminating agents." But Yang et al. (1992) observe that, "Since the pH of the Fichlor solution is about 6, detoxification of G-agents by this method is too slow to be effective."

6.2.3 Aqueous Chlorine Dioxide

Durst et al. (1988) have cited a 1969 internal Edgewood Arsenal research report to the effect that chlorine dioxide, ClO_2, reacts (rapidly) with VX to give carbon dioxide, carbonyl sulfide, sulfate ion, EMPA, and diisopropylamine. They have pointed out concerns with the "explosive nature" of the gas as a deterrent to large-scale work. However, chlorine dioxide is used extensively and safely on a large scale for paper pulp bleaching and for disinfecting municipal potable water supplies; the gas is generated in situ. There is considerable potential for chlorine dioxide to be used in the final step of the decontamination of equipment with basic aqueous solutions to ensure complete destruction of VX and any EA 2192 that might potentially be present in decontamination waste streams. Basic research on the reactivity of chlorine dioxide with amines (the class to which VX belongs) is summarized by Rosenblatt and Burrows (1982). Because of its small molecular size and low molecular weight, and because it is neither ionic nor very polar, chlorine dioxide might be able to penetrate into the interior of porous organic materials, such as paint or plastics, where it could react with absorbed agent. The potential exists (though no research has been done on this) for rapid chlorine dioxide reaction with mustard and related species (such as dithiane, thioxane, and thiodiglycol), though not with G-agents.

6.2.4 MCBD Microemulsion and German C8 Emulsion

The multipurpose chemical, biological decontaminant (MCBD) microemulsion consists of 60% water (the continuous phase), 7% tetrachloroethylene, 4% Fichlor, 28% of the surfactant n-cetyl trimethylammonium chloride, a small amount of the cosurfactant and phase transfer catalyst tetrabutylammonium hydroxide, 0.1% sodium 2-nitro-4-iodoxybenzoate (IBX, a nucleophilic catalyst for G-agent — but not VX — hydrolysis), and sodium borate buffer to maintain a pH of about 10 (Yang et al. 1992). This mixture was designed to decontaminate all agents of interest.

The German emulsion (C8) is composed, by weight, of 15% tetrachloroethylene (the continuous phase), 76% water, 1% anionic surfactant, and 8% calcium hypochlorite. Because the continuous phase is organic, this emulsion "is noncorrosive and as good a solvent as pure tetrachloroethylene for the thickened agents. In addition, C8 can penetrate into paint to dissolve and react with imbedded agent without damaging the paint. When the emulsion is sprayed, a thin, coherent film is formed on the surface to allow sufficient residence time for reaction with the agents" (Yang et al. 1992).

6.2.5 DANC

Typically, DANC (decontaminating agent, noncorrosive) consisted of about 7% of 1,3-dichloro-5,5-dimethylhydantoin or of 1,1'-methylenebis(3-chloro-5,5-dimethylhydantoin), both of which are chlorinating agents, in 1,1,2,2-tetrachloroethane (Chemical Biological Information Analysis Center 1993); there were evidently

several formulations. DANC was designed for use against H/HD, although it should also be effective against VX but not against G-agents. The chlorinating agent reportedly reacts with HD in aqueous solution "to give a sulfilimine derivative." Because 1,1,2,2-tetrachloroethane is toxic and has a corrosive effect on painted surfaces and rubber, DANC has become obsolete (Durst et al. 1988).

6.2.6 Future Directions

Yang et al. (1992) discuss decontaminants of the future, which would be noncorrosive; biodegradable; capable of penetrating agent thickeners; and effective against HD, VX, GB, and GD. Strong bases or calcium hypochlorite dissolved in mixtures of water with biodegradable N-alkyl-2-pyrrolidones seem to fit the requirements. It would appear that the dielectric constants of N-alkyl-2-pyrrolidones are high enough that these solvents should not decrease the rate-limiting formation of cyclic sulfonium salts by HD in aqueous mixtures. Also, these cyclic amides should resist oxidation, chlorination, and hydrolysis. An example of one such decontaminant (Decontaminating Agent: Multipurpose [DAM]) is 4% (by weight) of calcium hypochlorite in an equivolume mixture of N-cyclohexyl-2-pyrrolidone and water. (According to Hall [1994], the mixture is not stable and may undergo exothermic decomposition.) The DAM development project was terminated both because of deficiencies in DAM and because the majority of serious problems associated with DS-2 have been corrected (Harlacker et al. 1993).

7.0 ADVANTAGES AND DISADVANTAGES OF THE VARIOUS SYSTEMS

One disadvantage of the major decontaminants is their limited ability to penetrate many of the substrate materials (such as paint and plastics) in which the agents of concern might be found. This is especially true of water-based decontaminants. Sufficiently long contact of the decontaminants with such media, along with adequate liquid shearing, should permit diffusion of agent into the decontaminant.

Purely aqueous base has the advantage of introducing no potentially hazardous chemicals other than sodium hydroxide or carbonate, which can be easily neutralized to dilute brines. It would be most effective against GB and GD. With VX, dissolution would not be rapid, a very high concentration of hydroxide would be required to effect a reasonable reaction half-life (e.g., about 3 min at pH 13.5 and 25°C), and the toxic and stable EA 2192 would be formed; however, the latter, along with mercaptan, organic sulfide, organic disulfide, and amine, could probably be destroyed readily and rapidly by treating the collected waste with chlorine dioxide bubbled in as a gas. Provided there was sufficient base to neutralize evolved hydrochloric acid, pH would have virtually no effect on the rate of H/HD hydrolysis. In any case, the rate of chemical reaction would be governed by the extremely low rate of solution in water. Aqueous base is not to be recommended for decontaminating VX (except if post-treatment is added to destroy the EA 2192 that would be present) or H/HD.

The efficacy of aqueous base towards VX is notably enhanced by adding of hydrogen peroxide. (This is probably not true of its reactivity with H/HD.) Sodium perborate may be used in place of hydrogen peroxide (Hovanec et al. 1993).

Sodium hydroxide in mostly alcoholic solution (90% alcohol or more) would be an effective but unnecessarily powerful decontaminant for GB. It might have some advantage over purely aqueous base for GD, which is less soluble in water than GB. It would be particularly effective against VX for reasons of solubility because it reacts rapidly and because EA 2192 is not among the observable products. The presence of alcohol increases H/HD

solubility but depresses the rate of hydrolysis. Costs of alcoholic solvents must also be considered. The toxicity of simple alcohols, such as methanol, is probably of little concern because they are quickly degraded by soil microorganisms. Solutions of sodium hydroxide in 90 to 100% alcohol would be recommended for GD and VX decontamination and would be highly effective (though unnecessarily costly) for GB. They would not be recommended for H/HD.

Somewhat alkaline aqueous hypochlorite solutions or slurries should be acceptably effective against G-agents (although constituting somewhat of an overkill), V-agents, and H/HD; they are, however, rather corrosive (Hovanec et al. 1993). Collected decontaminating solutions would have to be neutralized, probably with stoichiometric amounts of sulfite.

Acidic solutions of hypochlorous acid would react rapidly with VX and be stoichiometrically more efficient than alkaline hypochlorite in converting the agent to harmless products. However, such solutions would tend to emit toxic and corrosive chlorine fumes that would have to be addressed by suitable engineering arrangements, including postdecontamination neutralization. Acidic chlorine solutions would not be very effective against G-agents; they would probably chlorinate H/HD to form products about which little is known.

Aqueous Fichlor is considered quite effective as a decontaminant for VX and perhaps for HD, but not for G-agents. As with other chlorinating decontaminants, the residual oxidizing power of excess Fichlor would have to be neutralized.

Chlorine dioxide rapidly detoxifies VX but does not react at all with G-agents. Its reactivity towards H/HD and their derivatives has not been tested. Because chlorine dioxide is a gas, its solutions can emit toxic and corrosive fumes requiring engineering controls. Reputed explosion hazards can easily be minimized. Excess chlorine dioxide can be reduced to either chlorite or chloride ion.

DS-2 solution is capable of decontaminating all the agents, though it has a limited capacity; it dissolves or softens some polymers and coatings, and it is combustible.

The tetrachloroethylene-based, active-chlorine-containing emulsions seem to be effective against the agents of concern but are toxic and expensive.

DANC was designed to use against H/HD but will also detoxify VX, though not GB or GD. It is damaging to many materials. The presence of 1,1,2,2-tetrachloroethane makes it toxic as well as costly.

The proposed new decontaminant, DAM, was thought to be effective, safe, and environmentally acceptable but is evidently too unstable to be kept for any length of time. It would probably also be expensive.

8.0 TOXIC REBOUND

The term "toxic rebound" is used primarily in connection with the generation of a small amount of GB when a brine containing the hydrolyzed salts from detoxification of GB with sodium hydroxide is spray dried (Epstein et al. 1977). The more concentrated the salt solutions are, the higher the acidity of the solution being spray dried and the higher will be the yield of GB. It was possible to generate low levels of GB even by mixing pure fluoride and methylphosphonate solutions (rather than by using GB hydrolysates). Epstein et al. (1977) observed that under

the spray-drying conditions in use, high concentrations of carbon dioxide were in contact with the material being treated, thus increasing the acidity of the brines. Heating the spray-dried solids also formed GB. The reformation phenomenon is of concern only when concentrations of the participating chemical species are high and heat is applied; it should not occur when these species are in dilute aqueous solution (especially high pH) or sparsely distributed among soil particles. Harris et al. (1982), developed an expression for the equilibrium between fluoride, isopropyl methylphosphonate ion, hydroxide ion, and GB with the objective of defining conditions under which the aqueous GB equilibrium concentration would not exceed 10^{-8}M, which they considered a safe limit:

$$[GB] = 10^{-19} [F^-] [IMP^-]/[OH^-]^2$$

At pH 7, then, $[GB] = 10^{-5} [F^-] [IMP^-]$, and, to conform to the safety criterion, $[F^-] [IMP^-] < 10^{-8}/10^{-5} = 10^{-3}$ M^2. This would indicate an initial safe GB concentration of $(0.001)^{0.5} = 0.032$ M, or 4.5 g per liter of decontaminating solution. For pH 8, that value would be increased a hundred fold. Dispersion of the GB hydrolysate in groundwater would dramatically reduce the potential level of reformed GB because the concentrations of both fluoride and methylphosphonate would be decreased. Complexation of fluoride with soil minerals would further diminish the potential for GB reformation.

In addition to the explanation for the detection of GB in brines resulting from GB hydrolysis, there is the strong possibility, demonstrated experimentally, of GB forming in neutralized or slightly acidic chloroform — but not methylene chloride — extracts of brines containing fluoride and isopropyl methylphosphonate (Beaudry et al. 1993). This represents an artifact in the analysis of brines by means of extraction followed by chromatography.

High concentrations of alkyl methylphosphonates (from hydrolysis of G-agents or VX) in dry soil might form somewhat toxic anhydrides; this would not occur to a serious degree in aqueous solution.

It is extremely unlikely that VX, once hydrolyzed, would form again under any conditions. However, one of the major hydrolysis products, diisopropylaminoethanethiol, would easily be air-oxidized to a reputedly vesicant disulfide. One sure way to prevent the occurrence of the latter product (as well as of EA 2192) is to decontaminate with chlorine, hypochlorite, or chlorine dioxide.

Thiodiglycol, the hydrolysis product of HD, can form HD by reaction with hydrochloric acid. In fact, a preparative method for HD consists of holding a mixture of one volume of thiodiglycol with three volumes of concentrated hydrochloric acid at 60°C for 30 min and collecting the heavy oil that precipitates (Bent 1947). The equilibrium concentration of HD is far lower near neutral pH, even when chloride ion is present (as it would especially be in certain saline soils). Unfortunately, the complex equilibria involved here have apparently not been adequately researched. It may be surmised that, over time, there should be a tendency to form irreversibly such products as oxathiane, 1,2-dichloroethane, and dithiane, thereby gradually lowering the potential for forming HD. It is true, as has already been reported in Section 3.5.2, that mustard can be formed (presumably in small yield) when its decomposition products — 1,4-dithiane and excess 1,2-dichloroethane — are heated in a sealed tube. However, such a reaction would not occur in the open because the volatile chlorocarbon would escape too quickly. Reformation of HD, then, is not at all likely under the conditions of basic hydrolysis, although more possible (to a small degree) at neutral pH. Oxidation with excess hypochlorite makes such a reaction utterly impossible.

Toxic rebound is primarily a problem with large-scale decontamination activities, and has little real-world relevance to the delisting process. Use of hypochlorite decontamination, moreover, completely precludes toxic rebound for HD and VX.

9.0 REFERENCES

Bartlett, P.D., and C.G. Swain, 1949, *Kinetics of Hydrolysis and Displacement Reactions of β,β'-Dichlorodiethyl Sulfide (Mustard Gas) and β-Chloro-β'-hydroxydiethyl Sulfide (Mustard Chlorohydrin)*, J. Am. Chem. Soc., *71*:1406-1415 (as cited by Yang et al. (1986)).

Beaudry, W.T., J.H. Buchanan, D.K. Rohrbaugh, J.B. Samuel, L.L. Szafraniec, and J.R. Ward, 1993, *Analysis of Decontamination Solutions of G Agents to Detect Reformation of Agent*, ERDEC-TR-005, Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, MD 21010, January. AD-A264308.

Bell, E.V., G.M. Bennett, and A.L. Hock, 1927, *Decomposition of Some Halogenated Sulphides, and the Nature of the "Polymeric" Ethylene Sulphides*, J. Chem. Soc., 1803-1809.

Bent, H.E., 1947, *The Laboratory Preparation of Mustard Gas*, Science, *106*: 374-375.

Bodek, I., W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, 1988, *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods*, Pergamon Press, New York.

Britton, K.B., and C.L. Grant, 1988, *Prediction of Octanol-Water Partition Coefficients of Organophosphonates. Evaluation of Structure-Function Relationships*, Special Report 88-11, U.S. Army Corps of Engineers Cold Regions Research & Engineering Laboratory, Hanover, NH, August.

Brooks, M.E., W.T. Beaudry, P.C. Bossle, R.E. Herd, J.M. Lochner, S.G. Pleva, J.H. Reeder, D.K. Rohrbaugh, T.E. Rosso, L.J. Szafraniec, and L.L. Szafraniec, 1994, *Operation Safe Removal: Spring Valley, Washington, D.C., Analytical Results: January-February 1993*, ERDEC-SP-008, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423, July. AD-A267804.

Carpenter, T.J., and T.E. Hill, 1988, *Methods for Demolition of Building E5625*, prepared by Battelle Columbus Division, Columbus, Ohio, for the U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, under Contract DAAA15-87-D-0011, Task 6, November.

Chemical Biological Information Analysis Center (CBIAC), 1993, *Nomenclature Guide for the Chemical Defense Materials Database (CDMD), Version 4.1*, Edgewood, MD, August.

Clark, D.N., 1989, *Review of Reactions of Chemical Agents in Water (Task 80), Final Report*, prepared by Battelle Columbus Division, Columbus, Ohio, for the U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD, under Army Project No. 88PP8847. AD-A213287.

Committee on Alternative Demilitarization Technologies, 1993, *Alternative Technologies for the Destruction of Chemical Agents and Munitions*, Board on Army Science and Technology, Commission on Engineering and Technical Systems, National Research Council, Washington, DC.

Cooper, W.A., 1990, *A Data Base on Persistent CW Agents on Terrain*, CRDEC-TR-204, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD. AD-B149 284.

Dacre, J.C., and W.D. Burrows, 1988, *Recommended Field Drinking Water Criteria for Chemical Agent Sulfur Mustard*, Technical Report 8816, U.S. Army Biomedical Research & Development Laboratory, Fort Detrick, Frederick, MD, December. AD-A221745.

D'Agostino, P.A., and L.R. Provost, 1985, *The Identification of Compounds in Mustard Hydrolysate*, Suffield Report No. 412, Defence Research Establishment, Suffield, Canada, April. CB-0008053.

Demek, M.M., G.T. Davis, W.H. Dennis, Jr., A.L. Hill, R.L. Farrand, N.P. Musselman, R.J. Mazza, W.D. Levine, D.H. Rosenblatt, and J. Epstein, 1970, *Behavior of Chemical Agents in Seawater*, Edgewood Arsenal Technical Report EATR 4417, Edgewood Arsenal Research Laboratories, Edgewood Arsenal, MD. AD-873242.

Dennis, W.H., Jr., L.A. Hull, and D.H. Rosenblatt, 1967, *Oxidations of Amines. IV. Oxidative Fragmentation*, J. Org. Chem., *32*:3783-3787.

Durst, H.D., E.W. Sarver, H.W. Yurow, W.T. Beaudry, P.A. D'Eramo, D.M. Jackson, H. Salem, L.L. Szafraniec, F.P. Ward, and J.R. Ward, 1988, *Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD02 in COMAR 10.51.02.16-1*, CRDEC-TR-009, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November. AD-A271648.

Edgewood Arsenal, 1968, *Purchase Description, Chemical Agent, GB, Redistilled* 196-21-86, FSC 1365, June 14.

Edgewood Arsenal, 1974, *Chemical Agent Data Sheets, Volume I*, Department of the Army, Aberdeen Proving Ground, MD, December. AD-B028222.

Epstein, J., V.E. Bauer, M. Saxe, and M.M. Demek, 1956, *The Chlorine-Catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate (Sarin) in Aqueous Solution*, J. Am. Chem. Soc., *78*:4068-4071.

Epstein, J., J.J. Callahan, and V.E. Bauer, 1974, *The Kinetics and Mechanisms of Hydrolysis of Phosphonothiolates in Dilute Aqueous Solution*, Phosphorus, *4*:157-163.

Epstein, J., G.T. Davis, L. Eng, and M.M. Demek, 1977, *Potential Hazards Associated with Spray Drying Operations*, Environ. Sci. Technol., *11*:70-75.

Eskanow, K., 1978. *Study on the Reaction of Methyl-O-Pinacolin-Phosphine Fluoride, Soman, with Calcium Hypochlorite in Aqueous Solution*, Biul. Wojsk. Akad. Tech., *27*:119-127 (1978); Chem. Abstr. *90*;44410w (1979).

Fuson, R.C., R.E. Foster, and R.D. Lipscomb, 1946a, *Levinstein Mustard Gas. VI. The Mode of Formation*, J. Org. Chem. *11*:504-509.

Fuson, R.C., R.D. Lipscomb, B.C. McKusick, and L.J. Reed, 1946b, *Thermal Conversion of Mustard Gas to 1,2-bis(2-Chloroethylthio)ethane and bis[2-(2-Chloroethylthio)-ethyl] Sulfide*, J. Org. Chem. *11*:513-517.

Fuson, R.C., C.C. Price, D.M. Burness, R.E. Foster, W.H. Hatchard, and R.D. Lipscomb, 1946c, *Levinstein Mustard Gas. IV. The bis(2-Chloroethyl) Polysulfides*, J. Org. Chem. *11*:487-498.

Hall, D., 1994, Personal communication with DH. Rosenblatt, *Stability of N-alkylpyrrolidone/ hypochlorite mixtures*, Dugway Proving Ground, Dugway, UT. December 19.

Harlacker, S.R., V.D. Auber, D.W. Macfarlane, T.M. Sotamayor, T.N. Nguyen, P.W. Bartram, J.W. Hovanec, J. Albizo, and V. Henderson, 1993, *Demonstration and Validation Phase Test and Evaluation of the Decontaminating Agent: Multipurpose (DAM)*, ERDEC-TR-125, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November. AD-B181883.

Harris, J.M., K. DeBruin, J.E. Gebhart, B.C. Garrett, and T.M. Prociv, 1982, *GB•NaOH Neutralization Mechanism and Analytical Procedures Evaluation*, Final Report, March-May 1982, DRXTH-SE-CR-82161, prepared for the U.S. Army Toxic and Hazardous Materials Agency under Contract No. DAAG29-81-D-0100, by Battelle Columbus Laboratories, Columbus, OH, July. AD-B067290.

Headquarters, Departments of the Army, Navy, and Air Force, 1990, *Potential Military Chemical/Biological Agents and Compounds*, Army Field Manual No. 3-9, Commandant, U.S. Army Chemical School, ATTN: ATZN-CM-NF, Fort McClellan, AL, December.

Healy, T.V., 1948, *Kinetics of the Hydrolysis of Pinacolyl Methanefluorophosphonate*, Porton Technical Paper No. 79, Porton Down, UK, November.

Hovanec, J.W., L.L. Szafraniec, J.M. Albizo, W.T. Beaudry, V.D. Henderson, Y.-C. Yang, B.K. MacIver, and L. Procell, 1993, *Evaluation of Standard and Alternative Methods for the Decontamination of VX and HD in Chemical Agent Disposal Facilities*, ERDEC-TR-054, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April. AD-A265 870.

Kingery, A.F., and H.E. Allen, 1993, *Extraction and Chromatographic Development of Selected Organophosphorus Compounds from Soil and Aqueous Media*, Final Report, prepared for the U.S. Army Environmental Center under Contract No. DAAL03-86-D-0001 by the University of Delaware, Newark, DE, January.

Kingery, A.F., and H.E. Allen, 1994, *Environmental Fate of Alkyl Methylphosphonates Arising from Chemical Surety Material (CSM) and Potential Non-CSM Sources in Soil and Aqueous Media*, Final Report, prepared for the U.S. Army Environmental Center under Contract No. DAAL03-86-D-0001 by the University of Delaware, Newark, DE, March.

Kingery, A.F., and H.E. Allen, 1995, *The Environmental Fate of Organophosphorus Nerve Agents: A Review*, Toxicology and Environmental Chemistry, *47*:155-184.

Kinnear, A.M., and J. Harley-Mason, 1943, *The Composition of Levinstein H*, Porton Report 2537, Military Intelligence Division, Great Britain, September.

Larsson, L., 1958, *A Kinetic Study of the Reaction of* iso*Propoxy-methyl-phosphoryl Fluoride (Sarin) with Hydrogen Peroxide*, Acta Chem. Scand., *12*:723-730.

Lyman, W.J., and C.P. Loreti, 1987, *Prediction of Soil and Sediment Sorption for Organic Compounds, Final Report*, Arthur D. Little, Inc., Cambridge, MA, prepared for the Monitoring and Data Support Division, Office of Water Regulations and Standards, U.S. Environmental Protection Agency, under Contract No. 68-01-6951, Task 15.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt, 1990, *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, American Chemical Society, Washington, DC.

MacNaughton, M.G., and J.H. Brewer, 1994, *Environmental Chemistry and Fate of Chemical Warfare Agents*, Final Report, SwRI Project 01-5864, Southwest Research Institute, San Antonio, TX, March.

Ogston, A.G., E.R. Holiday, J. St. L. Philpot, and L.A. Stocken, 1948, *The Replacement Reactions of β,β'-Dichlorodiethyl Sulphide and of Some Analogues in Aqueous Solution: The Isolation of β-Chloro-β'-Hydroxy Diethyl Sulphide*, Trans. Faraday Soc., *44*:45-52.

Penski, E.C., 1993, *The Properties of Di-(2-chloroethyl) Sulfide. I. Vapor Pressure Review and Analysis*, Technical Report ERDEC-TR-043, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April. AD-A267059.

Preston, J.M., and V. Starrock, 1983, *Partial Vapor Pressures and Activity Coefficients of GB and GD in Aqueous Solution*, Report 893, Chemical Defence Section, Protective Sciences Division, Defence Research Establishment, Ottawa, Canada, September. AD-A140644.

Rohrbaugh, D.K., 1994, *Personal Communication* "Analyses of mustard gas from an old munitions sample and from a sample of stored distilled mustard." U.S. Army Edgewood Research, Development and Engineering Center, November.

Rosenblatt, D.H., 1975, "Chlorine and Oxychlorine Species Reactivity with Organic Substances," in D.J. Johnson, ed., *Disinfection: Water and Wastewater*, Ann Arbor Science, Ann Arbor, MI.

Rosenblatt, D.H., and E.P. Burrows, 1982, "Oxidation of Amines," in S. Patai, ed., *The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Part 2*, Chapter 25, Interscience Publications, John Wiley & Sons, New York.

Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul, and D.R. Cogley, eds., 1975, *Problem Definition Studies on Potential Environmental Pollutants. II. Physical, Chemical, Toxicological, and Biological Properties of 16 Substances*, Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD. AD A030428.

Rosenthal, R.W., R. Proper, and J. Epstein, 1956, *The Distribution of Some Phosphonofluoridates between Organic Solvents and Water*, J. Phys. Chem., 60:1,596-1,598.

Sage, G.W., and P.H. Howard, 1989, *Environmental Fate Assessments of Chemical Agents HD and VX*, CRDEC-CR-034, prepared by Syracuse Research Corporation, Syracuse, NY, for the Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June. AD-B135352.

Samuel, J.B., E.C. Penski, and J.J. Callahan, 1983, *Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures (U)*, Special Publication ARCSL-SP-83015, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June.

Small, M.J., 1983, *Soil Detection Limits for Potential Chemical Warfare-Related Contaminants at Fort McClellan Alabama*, Technical Report 8208, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, May. AD-B077091L.

Small, M.J., 1984, *Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate*, U.S. Army Medical Bioengineering Research & Development Laboratory, Fort Detrick, Frederick, Md., Technical Report 8304, June. AD-A149515.

Szafraniec, L.J., L.L. Szafraniec, W.T. Beaudry, and J.R. Ward, 1990, *On the Stoichiometry of Phosphonothiolate Ester Hydrolysis*, CRDEC-TR-212, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, July. AD-A225952.

Szafraniec, L.L., W.T. Beaudry, and Y.-C. Yang, 1993, *Hydrolysis of VX and S-2-(Diisopropylamino)ethyl Methylphosphonothioic Acid (EA 2192) in Super-Alkaline Solution*, Proceedings, 1992 ERDEC Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 17-20, 1992.

U.S. Army, 1964, *Military Specification. Chemical Agent, VX*, MIL-C-51105A(MU) (as cited by Small 1983).

U.S. Army, 1969, *Military Specification. Chemical Agent*, GB, MIL-C-10758D(MU) (as cited by Small 1983).

U.S. Environmental Protection Agency, 1986, *Superfund Public Health Evaluation Manual, Appendix C*, EPA 540/1-86/060, Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC, October.

Witten, B., 1969, *The Search for Toxic Chemical Agents*, Technical Report EATR 4210, Edgewood Arsenal Research Laboratories, Edgewood Arsenal, MD, November.

Yang, Y.-C., J.R. Ward, and T. Luteran, 1986, *Hydrolysis of Mustard Derivatives in Aqueous Acetone-Water and Ethanol-Water Mixtures*, J. Org. Chem., *51*:2756-2759.

Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, and J.R. Ward, 1987, *Sulfonium Chlorides Derived from 2-Chloroethyl Sulfides. I. Formation and Magnetic Resonance Identification in Water*, CRDEC Technical Report TR-88008, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, October. AD-A187594.

Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, and D.K. Rohrbaugh, 1990, *Oxidative Detoxification of Phosphonothiolates*, J. Am. Chem. Soc., *112*:6621-6627.

Yang, Y.-C., J.A. Baker, and J.R. Ward, 1992, *Decontamination of Chemical Warfare Agents*, Chem. Rev., *92*:1729-1743.

Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, and C.A. Bunton, 1993a, *Perhydrolysis of Nerve Agent VX*, J. Org. Chem., *58*:6964-6965.

Yang, Y.-C., L.L. Szafraniec, and C.A. Bunton, 1993b, *Nucleophilic Substitution of O,S-Diethyl Methylphosphonothiolate: The Selectivity of P-S- to P-O Bond Cleavage*, Proceedings, 1992 ERDEC Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 17-20 1992.

Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, J.B. Samuel, and D.K. Rohrbaugh, 1994, *Hydrolysis of VX: Activation Energies and Acid Catalysis* (Oral Presentation), 1994 Scientific Conference on Chemical and Biological Defense Research, Aberdeen Proving Ground, MD, November 15-18.

Yurow, H.W., 1981, *Decontamination Methods for HD, GB and VX. A Literature Survey*, ARCSL-SP-80032, AD B057399L (as cited by MacNaughton and Brewer 1994).

APPENDIX A

SYMBOLS AND ACRONYMS

a	Constant for a given temperature and polymer-solvent system
Argonne	Argonne National Laboratory
atm	Atmospheres pressure; 1 atm is equivalent to 760 torr
C	Point concentration
cal	calorie
CAS	Chemical Abstracts Services
CFR	Code of Federal Regulations
CH-TG	$HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S^+(CH_2\text{-}CH_2\text{-}OH)_2$, mustard chlorohydrin-thiodiglycol complex
C8	German emulsion (see Section 6.2.4)
d	Day, unit of time; or density in g/cm^3
D	Diffusion coefficient for a specific concentration of permeant in a polymer
D_0	Zero-concentration diffusion coefficient
DAM	Decontaminating agent: multipurpose
DANC	Decontaminating agent, noncorrosive
DDP	Diethyl dimethylpyrophosphonate
DEOH	2-Diisopropylaminoethanol
DEQ	Department of Environmental Quality (State of Utah)
DESH	2-Diisopropylaminoethanethiol
$(DES)_2$	Bis(2-Diisopropylaminoethyl) disulfide
$(DE)_2S$	Bis(2-Diisopropylaminoethyl) sulfide
DIMP	Diisopropyl methylphosphonate
DIPC	Diisopropyl carbodiimide
DIPU	N,N'-Diisopropylurea
DPG	U.S. Army Dugway Proving Ground
DS-2	Decontamination Solution 2

DSHW	Department of Solid and Hazardous Waste (State of Utah)
EA 2192	S-(2-Diisopropylaminoethyl) methylphosphonothioic acid
EA 4196	See $(DES)_2$
EMPA	Ethyl methylphosphonic acid
EMPS	Ethyl methylphosphonothioic acid
EPA	U.S. Environmental Protection Agency
f_{oc}	Fraction of organic carbon in a given soil
F999	Residues from demilitarization, treatment, and testing of nerve, military, and chemical agents
g	Gram
GB	Agent sarin, isopropyl methylphosphonofluoridate
GC/MS	Gas chromatography/mass spectrometry, an analytical methodology
GD	Agent soman, pinacolyl methylphosphonofluoridate
GLC	Gas-liquid chromatography
h	Hour, unit of time
H	Crude sulfur mustard agent, bis(2-chloroethyl) sulfide
HD	Distilled sulfur mustard agent
HD-O	Mustard sulfoxide
$HD\text{-}O_2$	Mustard sulfone
HOCl	Hypochorous acid
H-TG	$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S^+ (CH_2\text{-}CH_2\text{-}OH)_2$, mustard-thiodiglycol complex
HTH	High-test hypochlorite, $Ca(OCl)_2$
H-2TG	$S[CH_2\text{-}CH_2\text{-}S^+ (CH_2\text{-}CH_2\text{-}OH)_2]_2$, mustard- bis(thiodiglycol) complex
IBX	Sodium 2-nitro-4-iodoxybenzoate
IMP	Anion of IMPA
IMPA	Isopropyl methylphosphonic acid
IRP	Installation Restoration Program
K_a	Acid dissociation constant

K_H	Henry's Law constant, ratio of the concentration of a compound in the vapor state to its concentration in a solvent (here, water) in a system at equilibrium
k_{obs}	Observed first order kinetic rate constant, in units of $(time)^{-1}$
K_{oc}	Soil organic carbon/water partition coefficient, ratio of concentration of a compound in soil organic carbon to its concentration in water in a system at equilibrium
K_{ow}	Octanol/water partition coefficient, ratio of concentration of a compound in n-octanol to its concentration in water in a system at equilibrium
K_w	Ion product of water (about 10^{-14} at 25°C)
k_2	Second order kinetic rate constant, in units of M^{-1} $(time)^{-1}$
L	Liter
L	Thickness of a polymer parallel to the direction of diffusion
LDPE	Low-density polyethylene
log	Logarithm to base 10
m	Meter, a fundamental unit of length
M	Molar, concentration of a substance in a given medium, expressed in moles per liter
M^{-1}	Liters per mole
MCBD	Multipurpose chemical, biological decontaminant (a microemulsion)
mg	Milligram, one thousandth of a gram
min	Minute, unit of time
mm	Millimeter, 1/1,000 m
mol	Mole, number of molecules in one gram-molecular weight of a substance, 6.022×10^{23}
MPa	Millipascal
MPA	Methylphosphonic acid
MW	Gram molecular weight
NMR	Nuclear magnetic resonance (a spectrometric method of chemical analysis)
obs	Observed
P	Vapor pressure
pH	Negative logarithm of the hydrogen ion activity (or concentration) in a solution: the higher the pH, the less acidic (more basic) is the solution
pK_a	Negative logarithm of K_a

PMPA	Pinacolyl methylphosphonic acid
PVC	Polyvinyl chloride
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
s	Second, unit of time
S	Solubility
SBR	Styrene-butadiene rubber
SOC	Soil organic content
t	Temperature, degrees Celsius; t = T - 273.16
T	Temperature, degrees Kelvin; or Ton
TECOM	U.S. Army Test and Evaluation Command
torr	Unit of pressure = 1 mm of mercury
tsat	Pseudosaturation time
$t_{½}$sat	½ tsat
VX	O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate
δ	Solubility parameter for a liquid in a polymer
μg	Microgram, one millionth of a gram
X	Flory interaction parameter
[X]	Concentration of chemical X in a particular medium

APPENDIX B

ENVIRONMENTAL FATE OF GB, VX AND HD

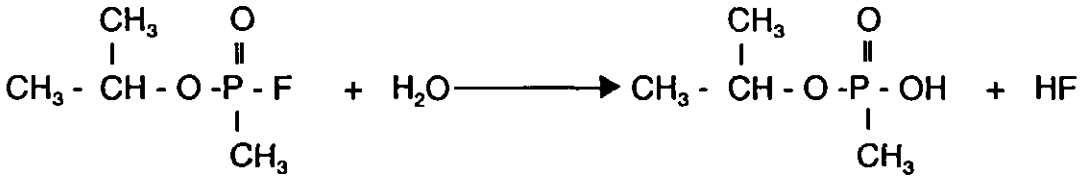
B-1.0 INTRODUCTION

The history of outdoor testing of agents GB, VX, and H/HD at DPG, which was discontinued in the 1960s, suggests that unconfined soil in agent test areas may have been contaminated with one or more of these agents. In addition, decontaminated materials may have been landfilled. It may be assumed that soils, assuming they originally contained agent, may not have been treated to decontaminate them. On the other hand, they have not been in a continually moisture-free condition that might have protected them from hydrolysis. The purpose of this Appendix is to describe the processes whereby the agents that may have been present originally might have degraded or dispersed. In the case of unconfined soil, the more water-soluble agents, their products, or their impurities could have then migrated away (while continuing to decompose) from the original site. Such migration usually results from dissolution and vertical (downward) movement in recharge water in the unsaturated zone or through nearly horizontal flow as dissolved material in the groundwater. Further, more volatile agents or breakdown products are capable of diffusing as vapors in the unsaturated zone until they escape to the soil surface and are dispersed by the wind.

B-2.0 GB AND ASSOCIATED COMPOUNDS

B-2.1 GB

GB undergoes loss from unconfined soils by evaporation, leaching, and hydrolysis. The initial hydrolytic reaction is:



GB **IMPA**

For the disappearance of GB from soil open to the air, Small (1984) cited a study by Puzderliski (1980). Samples of soil were placed in 7-cm diameter open crystallizing flasks. On each sample, drops of GB were placed corresponding to a nominal surface density of 50 g/m^2, a rather heavy loading. The flasks were buried at ground level in outdoor soil where they were exposed to weathering. During the exposure period, samples were assayed. (The methods of assay were not well documented.) The time frame of interest was the period, τ, required for the agent density to decrease to 0.033 mg/m^2, i.e., by a factor of 1500, somewhat over 10 half-lives. Puzderliski derived the values of τ shown in Table B-1.

Table B-1. Persistence Times Predicted for GB Droplets on Soil

(τ, hours)

Temperature °C	Calm, dry	Windy, dry	Light rain	Heavy rain
0	274	238	434	279
25	8.9	7.8	14.2	9.1

"Closed container" studies essentially preclude evaporative or leaching effects; any decrease in content of a contaminant in the soil may be attributed to chemical interaction in the soil, such as hydrolysis, chemisorption, air oxidation, or soil-catalyzed reactions, with no displacement of equilibria through removal of products. Contaminated samples are stored in the containers at room temperature and periodically assayed (Small 1983). Sass et al. (1953) conducted a closed-container study of GB decomposition in loam of pH 6.5 and in humus, pH 4.5, at room temperature, which one may consider to be 21°C. The percent GB remaining after given periods was determined (Table B-2). Percent GB vs. time in this study was generally linear for the first 24 h. Especially in the moist loam, the degradation rate was considerably faster than it would have been in water at the same pH and temperature; thus, in water at pH 6.5 and 21°C, according to Larson's equation (see below), the half-life is calculated as 394 h. When soil containing 1% moisture was contaminated with GB, 13% could be recovered in 3 days, 2.6% in 7 days, and 0.02% in 35 days (USATECOM undated). A model developed for the fate of GB in Lakewood Sand soil indicated a half-life of about 13 h for what is presumed to have been 50 mL of aqueous GB (initially 4 mg/L) shaken with 2 g of the soil at room temperature (about 21°C) (Kingery and Allen 1994).

Table B-2. Percent GB Remaining at Indicated Time After Application (hours)

	Hours				
Soil (% Moisture)	12	24	48	72	168
Humus (2.9)	56	28	9	2	Nil
Humus (36.8)	42	Nil	Nil	--	--
Loam (1.4)	59	27	14	12	5
Loam (12.8)	40	Nil	--	--	--

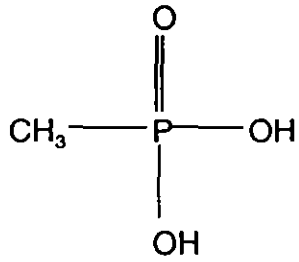
The half-life for GB in water decreases linearly with increasing [OH^-] from about pH 6.5 upward and decreases linearly with increasing [H_3O^+] from about pH 4 downward. In the pH 4-6.5 interval, aqueous GB is at its most stable, with a half-life at 25°C of about 238 h (see graphic presentation by Kingery and Allen 1994); the half-life at pH 3 is about 18 h. For pH values above 6.5, the following equation (Kingery and Allen 1995, as derived from Larsson 1957) may be used to estimate half-life in fresh water: log $t_{½}$ (hours) = 5039/T - pH - 8.035, where T is temperature (degrees Kelvin). The presence of magnesium and calcium ions in seawater considerably accelerates GB hydrolysis; thus, at pH 7.7 and 15°C, the experimental half-life is 2.65 h (Epstein 1970), compared to the estimate of 56.5 h by Larsson's equation for water free of catalytic metal ions. Other metallic ions also catalyze the hydrolysis of GB.

Minute amounts of GB might remain at equilibrium in the soil-water system, but the chances that detectable quantities of agent are present as the result of agent dissemination in a former military testing program are exceedingly small. It may be concluded that under the worst plausible conditions, dispersed GB in contact with relatively dry (but not totally water-free) soil would not be detectable in the soil after about 15 half-lives, with the half-life seldom exceeding about 2 days. Thus, soil originally contaminated with dispersed GB should be free of detectable agent after a month or less.

B-2.2 GB Hydrolysis Products

Fluoride ion (F^-), present as its salts, is nonvolatile and, in aqueous solution, is not retarded through sorption mechanisms as it is transported through the soil. The concentration of fluoride ion in soils worldwide is in the range of 20-700 mg/kg, with a median value of 200 mg/kg (Bodek et al. 1988).

Soil sorbs isopropyl methylphosphonic acid (IMPA) to a significant degree (Kingery and Allen 1994); this implies that, depending on the soil type, leaching may be retarded by the soil to some extent. The hydrolysis rate for IMPA in aqueous solution at ambient temperature is extremely slow; yet, in certain soil-water systems, appreciable hydrolysis to methylphosphonic acid (MPA) takes place. For example, 50 mL of aqueous IMPA (4 mg/L) shaken with 2 g of Fort McClellan clay loam soil had a half-life of 2.9 h (presumably at about 21°C); however, aqueous IMPA shaken with sandy clay loam from Dugway Proving Ground or sandy loam from Rocky Mountain Arsenal showed no observable hydrolysis (Kingery and Allen 1994). Thus, it would be possible that MPA would be found in the vicinity of former GB dissemination as a secondary hydrolysis product of the agent. Moreover, MPA is degraded by some microorganisms to inorganic phosphate; but the process is usually quite slow and may not occur everywhere (Kingery and Allen 1994). Aqueous IMPA and MPA were routinely analyzed in water down to a level of 0.5 µg/L by ion chromatography (Kingery and Allen 1993). It may be concluded that the most likely long-lived products of GB hydrolysis in soils would be fluoride ion and MPA.



MPA

B-2.3 GB Impurities and Stabilizers

Methylphosphonic difluoride, a potential impurity of GB, rapidly hydrolyzes to MPA (see above) and fluoride ion on exposure to water.

Another GB impurity, diisopropyl methylphosphonate (DIMP), undergoes extremely slow aqueous hydrolysis to IMPA (see above) and isopropyl alcohol. By extrapolation of results from high-temperature hydrolysis, it was estimated that the half-life of DIMP in groundwater at 10°C would be about 687 years (Rosenblatt et al. 1975). The fairly high boiling point of DIMP, 174°C (Rosenblatt et al. 1975), suggests that the compound would not readily disappear from soil or groundwater by evaporation. The presence of DIMP in Rocky Mountain Arsenal groundwater over several decades tends to confirm the perception that DIMP disappears very slowly from the environment.

Diisopropyl carbodiimide (DIPC), which was added as a stabilizer for weapons-grade GB, is hydrolyzed to N,N'-diisopropylurea (DIPU). Williams and Ibrahim (1981) measured the observed pseudo-first-order rate constant (units of s^{-1}) at 25°C and 1 M ionic strength, over a range of pH values, to obtain the equation

$$k = 63\,[H^+] + 0.0011\,[OH^-].$$

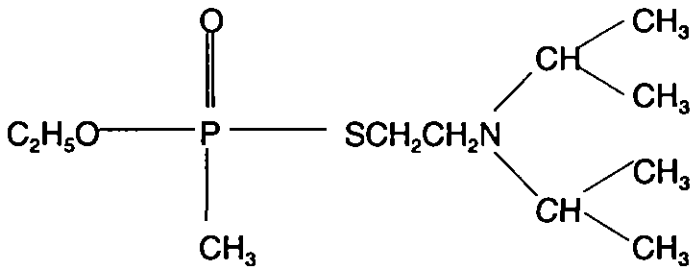
From the equation, one calculates that the half-life at pH 7 would be 31.6 h; the longest half-life, at pH 9.4, would be about 3,600 h.

The GB stabilizer tributylamine, which boils at 213°C (Weast 1979), is not expected to volatilize readily. It cannot hydrolyze.

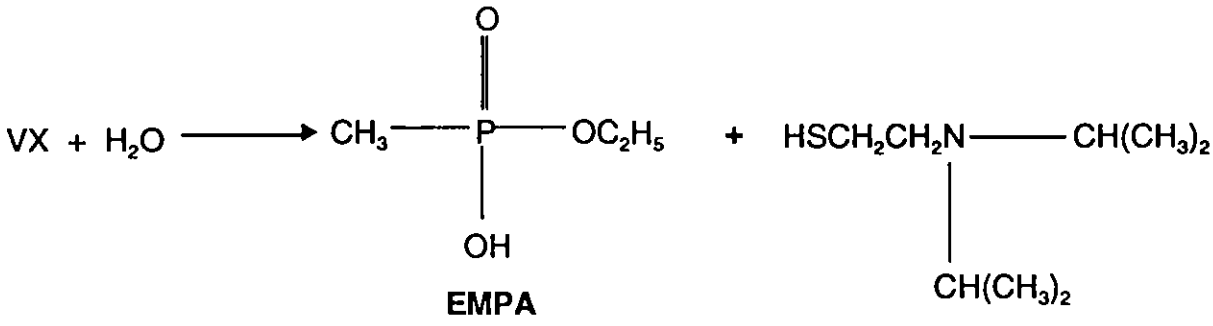
In summary, aside from compounds that are also products of GB hydrolysis, the most likely long-lasting environmental contaminants arising from GB stabilizers and impurities would be N,N'-diisopropylurea, tributylamine, and DIMP.

B-3.0 VX AND ASSOCIATED COMPOUNDS

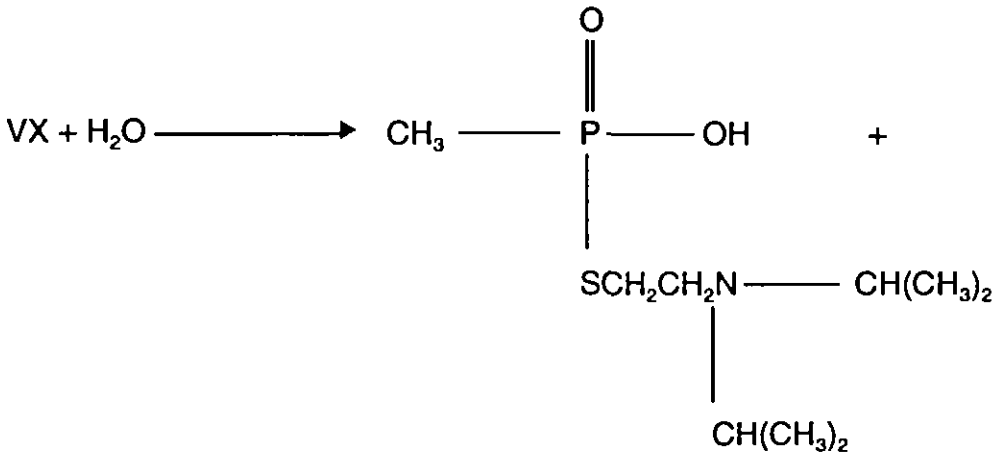
B-3.1 VX



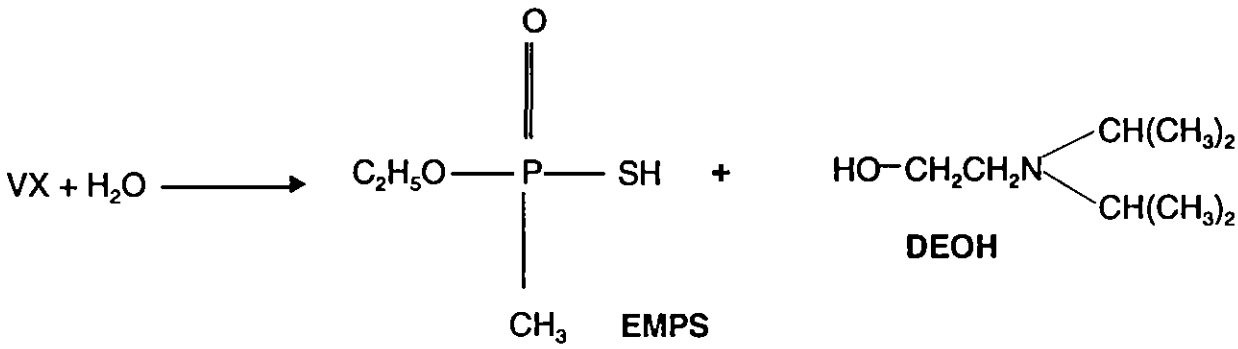
It is likely that VX undergoes loss from unconfined soils mainly by leaching and to a lesser extent by hydrolysis and evaporation. Three major initial hydrolytic reactions can occur (Epstein et al. 1974):



EMPA **DESH**

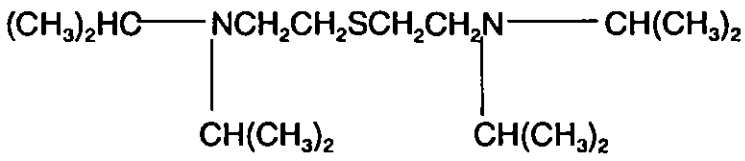


EA 2192



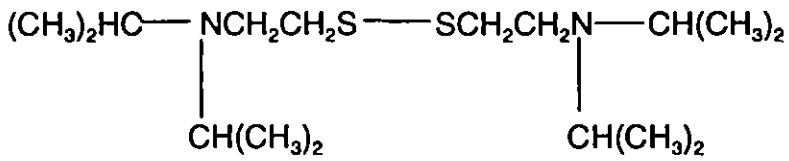
EMPS **DEOH**

In addition, a cyclic imonium intermediate in the last of the above reactions can interact with DESH to form



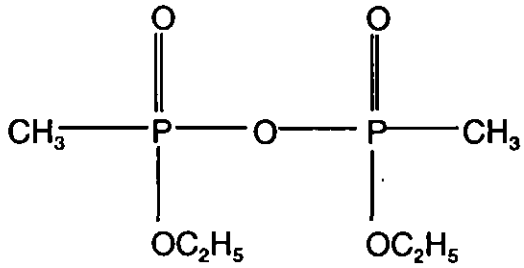
$(DE)_2S$

DESH is rapidly air-oxidized (Kaaijk and Frijlink 1977) to the environmentally stable disulfide, $(DES)_2$ or EA 4196.



$(DES)_2$

Finally, under environmental conditions, it appears that VX can react with the anion of EMPA to form the anion of DESH plus a cholinesterase inhibitor, the pyrophosphonate DDP (Small 1983):



Diethyl dimethylpyrophosphonate (DDP)

For the disappearance of VX from soil open to the air, Small (1983) cited a study by Demek and Epstein (1959) that describes a small-scale 1957-1958 study of the fate of VX on Carroll Island soil plots. Samples of soil were tested 17 to 52 days after VX application; about three orders of magnitude decrease in VX soil content was observed. Small (1984) cited a report by Griffiths et al. (1979) on analysis of samples taken from the Dugway Proving Ground V-Grid area. At some time before 1969, VX had been tested at this site and soil samples had shown VX levels as high as 6 mg/g. The 1979 tests at depths down to 102 cm indicated no VX at detection levels as low as 0.4 µg/g. The degradation product MPA (see Section B-2.2) was found at concentrations ranging from 14.9 to 23 µg/g; no $(DES)_2$ was detected.

Epstein et al. (1959) conducted a closed-container study (see definition above) of VX in soil. In these tests, 0.1 g of VX was added to 10-g samples of Carroll Island soil (fine silty loam, pH 6.5,SOC = 0.8%) in glass-stoppered flasks. Moisture content was 4.5%, 20%, or 50%. With little effect by percent moisture, the VX level dropped to 2.5-7.2% of its initial value in 14 days, as measured by cholinesterase inhibition. The recorded rate

of disappearance of VX decreased with time, but this could have been due to the formation of cholinesterase-inhibiting products (e.g., EA 2192). A follow-on study with different soils essentially confirmed the results (Demek and Epstein 1959). Studies at the Netherlands' TNO Laboratories involved application of 200 mg/kg of VX to soil (Verweij and Boter 1976; Kaaijk and Frijlink 1977). After 3 weeks, only 0.1% of the applied VX was detectable. EA 2192 was observed within a day after VX introduction to the soil but was found to degrade about as rapidly as VX. EMPA was the main initial phosphorus-containing product, and it slowly degraded to MPA. In USATECOM studies, when soil containing 1% moisture was contaminated with VX, 21% could be recovered in 3 days and 10% in 15 days (USATECOM undated).

The half-lives for disappearance of VX at 25°C in aqueous solution have been reported by Epstein et al. (1974) as shown in Table B-3 (where some of the values were actually determined for the diethylamino analog of VX, which has virtually identical hydrolytic behavior).

Table B-3. Hydrolysis Half-Lives for VX (Epstein et al. 1974)

pH	Half-Life (hours), 25°C
2.0	2,520
4.0	2,257
6.0	2,381
7.0	996
8.0	184
9.0	63
10.0	40.5
11.0	15
12.0 (approximately 0.01 M NaOH)	2.5
12.65	0.525
12.9	0.279
13.5	0.0529

Because VX is a base, the pH resulting from its dissolution in water is sufficient to initiate its own hydrolysis. However, the acid generated by that reaction would gradually lower the pH, so that the apparent half-life would decrease with time. Yang et al. (1990) estimated 80 h as the "half-life for the spontaneous hydrolysis" of VX at 20°C. Szafraniec et al. (1990) made a 0.5% solution of VX in unbuffered water; the initial pH was 9.0, and this dropped to 7.5 in the course of hydrolysis" The overall first-order rate constant was 0.0121 h^{-1}, so that the half-life was 57 h. Cleavage fractions were P-O, 0.54 (product EA 2192); P-S, 0.36; and S-C, 0.10. Thus, cleavage to produce EA 2192 was dominant under these conditions.

With the exercise of a certain amount of judgment, it may be concluded from the foregoing that under the worst plausible conditions, dispersed VX in contact with relatively dry (but not totally water-free) soil would not be detectable in the sample after about 3 months.

B-3.2 VX Hydrolysis Products

Information on most VX hydrolysis products is sparse.

The hydrolysis product ethyl methylphosphonate may be assumed to have an environmental fate very similar to that of isopropyl methylphosphonate (see Section B-2.3).

As noted above, the hydrolysis product DESH is rapidly air-oxidized (Kaaijk and Frijlink 1977) to the environmentally stable $(DES)_2$, which is rather tightly bound to the soil. It is reasonable to assume that $(DE)_2S$ is also tightly bound.

Verweij and Boter (1976) reported the rapid hydrolysis of DDP ($t_{½}$ = 1 h).

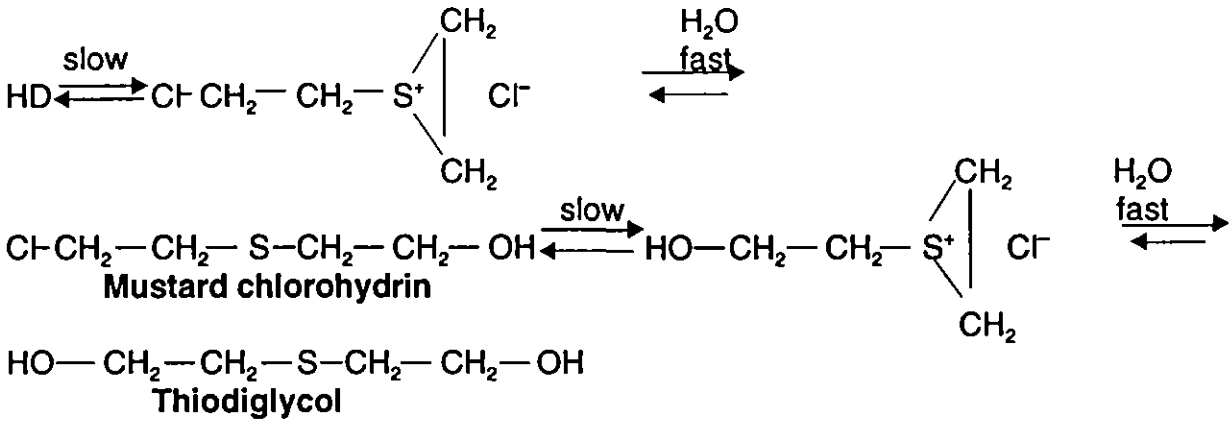
Under very alkaline conditions, the half-lives (in minutes) of VX and EA 2192 can be expressed as $t_{½} = 2.17/([OH^-]^{1.2})$ and $t_{½} = 835/[OH^-]^{1.6}$, respectively (Szafraniec et al. 1993). This indicates that EA 2192 should be considerably more stable in water than VX. Nevertheless, it appears to degrade as readily as VX in soil (see above).

It is concluded that the most long-lasting products of VX decomposition in weathered soil samples would be $(DES)_2$ and MPA.

B-4.0 HD AND ASSOCIATED COMPOUNDS

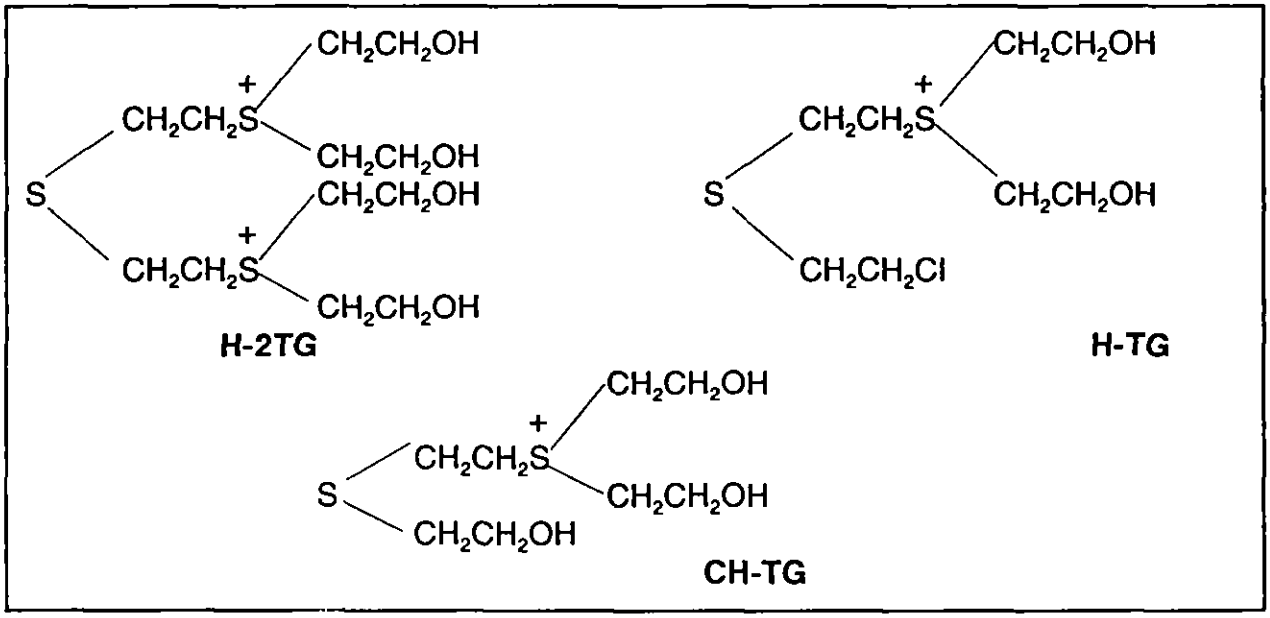
B-4.1 HD, $Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$

The following reactions of HD with water are observed almost exclusively when the ratio of water to HD is relatively high (Rosenblatt et al. 1975):



If chloride ion is present, as it is in seawater, for example, the hydrolysis reaction is retarded because chloride ion reacts with the cyclic sulfonium intermediates to reform HD. Strong nucleophiles, for example thiosulfate, also react with the cyclic intermediates, competing with water or hydroxide for them, and thereby diminishing the yield of thiodiglycol (Ogston et al. 1948).

In addition to the foregoing, there are other reactions in water-containing media. These involve alkylation of sulfide to linear sulfonium ions and dealkylation of the latter, leading to a large number of quasi-stable sulfonium ion intermediates (Yang et al. 1987), such as H-2TG, H-TG, and CH-TG. Ions of this type retain much of the toxicity of mustard, including its vesicancy (Yang et al. 1987). Thus, reaction of HD with limited volumes of water can result in the loss of HD without corresponding loss of toxicity. Most analytical procedures used to examine soil or groundwater cannot detect ionic products such as these.



Finally, some end products from the series of alkylation and dealkylation reactions are readily measured in either organic or aqueous media. Aside from thiodiglycol (mentioned above), 1,4-oxathiane is formed when water is present. In dry HD, thermochemical reactions (most likely via alkylation and dealkylation) lead to 1,4-dithiane and 1,2-dichloroethane (Bell et al. 1927). The latter, especially, is fairly volatile, boiling at 83°C (Weast 1979); in the open, it quite likely volatilizes over a period of time, displacing any slow equilibrium that might tend to reform HD.

Despite the rapidity with which the hydrolysis reaction occurs (once the HD is in aqueous solution), there is reason to believe that a tendency exists, in quiescent conditions, for HD to polymerize at the HD/water interface, interfering with transfer of HD to the aqueous solution and thus shielding the bulk agent from hydrolysis reactions (MacNaughton and Brewer 1994). Hence, the fact that bulk HD (or H) can persist deep in the soil or under relatively quiescent water for years may be due to encapsulation by oligomeric degradation products of limited hydrolysis, which are related to the linear sulfonium ions shown above. Small (1984) points out that each $-SC_2H_4-$ unit of increase in oligomer or polymer chain length would increase the octanol-water partition coefficient by a factor of 1.6; there would be some corresponding decrease in the aqueous solubility of the oligomer (which could itself be quite toxic). Samples of soil or groundwater taken near an encapsulated HD mass might show no trace of the active agent. The Committee on Alternative Demilitarization Technologies (1993) state: "The chemical problem is that the intermediate products are cyclic or oligomeric sulfonium salts, which are relatively unreactive and which moreover have the potential for slowly reforming mustard." Yang et al. (1987) express the belief that "the enduring toxicity of mustard gas in the environment can hardly be explained unless additional transformations of mustard gas into stable products of similar toxicity exist."

The impurities found in H, such as the polysulfides, might be expected to hinder the already slow dissolution of the agent, and, if they dissolved in water, to react more slowly with water than HD (or not at all). One impurity, 1,2-bis(2-chloroethylthio)ethane ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$), is about five times as vesicant as HD itself; others, such as 1,8-dichloro-3-oxa-6-thiaoctane ($Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}Cl$), are probably about as toxic as HD. Yet others, perhaps including the HD polysulfides, might be considerably less vesicant.

Small (1983) has cited field plot and shell explosion tests in which the time required for the air concentration of HD to drop to 10% of the initial value varied from 5 h to 10 days. If one assumed that such measured HD concentrations in air corresponded directly to those in the soil, it would follow that soil HD levels were reduced 90% in the same time range. For the disappearance of HD from soil open to the air, Small (1984) cited the study by Puzderliski (1980). Samples of soil were placed in 7-cm diameter open crystallizing flasks. On each sample, drops of HD were placed corresponding to a nominal surface density of 50 g/m^2, a rather heavy loading. The flasks were buried at ground level in outdoor soil where they were exposed to weathering. During the exposure period, samples were assayed. (The methods of assay were not well-documented.) The time frame of interest was the period, τ, required for the agent density to decrease to 0.033 mg/m^2, i.e., by a factor of 1500, somewhat over 10 half-lives. Puzderliski derived the values of τ shown in Table B-4.

Table B-4. Persistence Times Predicted for HD Droplets on Soil

(τ hours)

Temperature °C	Calm, dry	Windy, dry	Light rain	Heavy rain
0	1,530	1,743	2,215	1,122
25	41.5	7.3	51.2	30.5

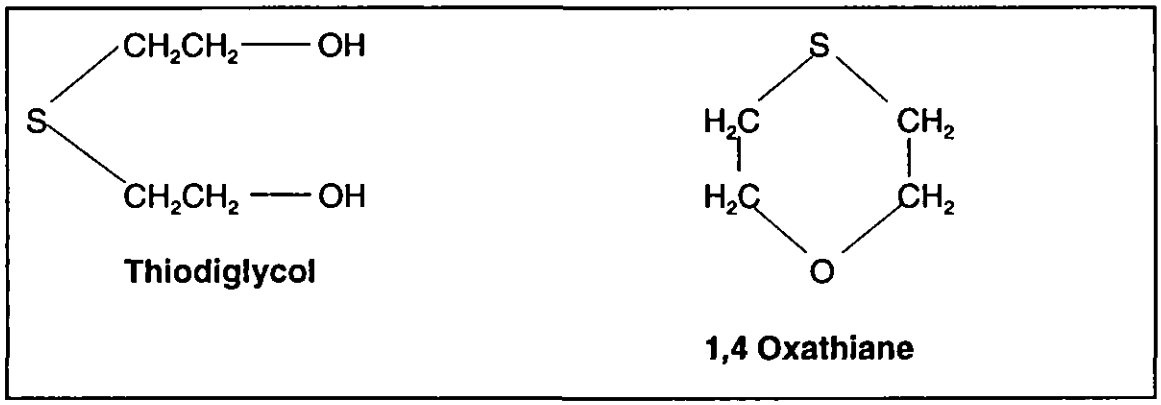
Small (1984) comments that "If HD droplets were applied to a soil surface, but not deliberately incorporated into the soil, vaporization could be the main route of HD loss. If the soil were extremely wet, hydrolysis might occur to an appreciable extent. If droplets were considerably below the soil surface, conditions similar to that of a droplet in quiescent water might prevail, and HD would persist (as HD or in oligomeric form)."

With the exercise of a certain amount of judgment, it may be concluded from the foregoing that even under cold weather conditions, fine droplets of HD in contact with surface soil would not be detectable after about a year. However, buried HD pockets of sufficient mass might survive for greater lengths of time and be difficult to detect.

B-4.2 HD Hydrolysis Products

Thiodiglycol, the major hydrolysis product of HD, is quite polar, being infinitely miscible with water and fairly high-boiling — 280°C at atmospheric pressure (Nemeth 1989), 164°C at 20 torr, and 133°C at 1 torr (Weast 1979); the octanol/water partition coefficient is 0.83 (Major 1989), also indicative of quite high polarity. Though it does not hydrolyze further, thiodiglycol can undergo environmental biodegradation. Two bacterial strains isolated from "local soil" (presumably at the Edgewood Area of Aberdeen Proving Ground) were able to use thiodiglycol as a sole source of carbon for growth: Pseudomonas pickettii strain SH18 and Alkaligenes xylosoxidans ssp. xylosoxidans strain SH42. In 72 h, the SH42 culture metabolized at least 97% of the organic starting material (hydrolyzed HD) to inorganic products. In the case of the SH18 culture, there was a 16% production of thiodiglycol sulfoxide, a product of "dead end" metabolism (Harvey et al. 1992).

1,4-Oxathiane melts at -17°C and boils at 147-150°C (Berkowitz et al. 1978). The octanol/water partition coefficient is 5.9 (Major 1989), indicating a compound of fairly high polarity. Berkowitz et al. (1978) calculate an aqueous solubility of approximately 167,000 mg/L. A vapor pressure of 5.3 torr at 25°C was estimated (Berkowitz et al. 1978). 1,4-Oxathiane is a groundwater contaminant often associated with production and demilitarization of H or HD, probably from hydrolytic decomposition (Roberts and Hartley 1992).



In summary, well-dispersed HD should be hydrolyzed in the environment mainly to thiodiglycol and 1,4-oxathiane.

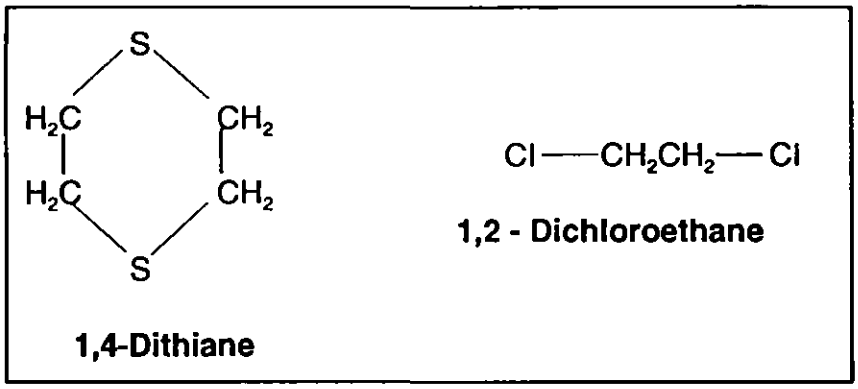
B-4.3 HD Impurities

1,4-Dithiane melts at 111-112°C and boils at 199-200°C (Weast 1979). The octanol/water partition coefficient is 71 (Major 1989), indicating a compound of considerably lower polarity than 1,4-oxathiane. Berkowitz et al. (1978) estimate an aqueous solubility of 11,800 mg/L and report an empirical vapor pressure equation of:

$$\log P \text{ (torr)} = 7.99 - (2{,}410/T(K)).$$

Thus, the vapor pressure at 25°C is approximately 0.8 torr. 1,4-Dithiane is a groundwater contaminant associated with H or HD storage and deposits; the occurrence of 1,4-dithiane is thought to result from mustard degradation (presumably thermal), because its concentration in HD increases with storage time (Roberts and Hartley 1992; Berkowitz 1982).

1,2-Dichloroethane is a product of the thermal decomposition of HD but by no means unique to that source. It is low-melting (-35°C) and low-boiling (83°C), with a vapor pressure of 79 torr at 20°C. Water solubility is 8,524 mg/L. The octanol/water partition coefficient of 30 indicates that it is not very polar. However, it is not expected to adsorb well to soil, in which it should exhibit high mobility. 1,2-Dichloroethane does not undergo environmental biodegradation to any great extent; most of it in soil or groundwater evaporates. Once in the atmosphere, it can travel long distances, eventually degrading through the action of photochemically formed hydroxyl radicals, with an atmospheric half-life of about a month (Howard 1990). One may conclude that 1,2-dichloroethane initially associated with environmental HD would tend to escape, primarily by evaporating.



B-5.0 EMISSION OF CONTAMINANTS FROM SOIL, TIME-AVERAGED FLUX ANALYSIS

Worst-case scenarios have been examined for the emission of agents GB, VX, and HD from soil in a landfill or other open disposal site. These estimates disregard chemical degradation, chemical binding to soil components (mineral or organic matter), and leaching as mechanisms for attenuation despite strong indications of such effects (see above). The basic model (Small 1993) is an adaptation of the equations developed by the EPA (Office of Remedial Response 1988); it takes into account the presence in soil of both air-filled and water-filled voids, as well as organic matter, which is especially important for the sorption of organic compounds of low polarity. The model assumes the initial presence of a layer of uniformly contaminated soil overlain by a layer of clean soil; diffusion of the contaminant occurs only upward.

Equation factors (Table B-5) include (1) site/soil/scenario-related default values and (2) contaminant-specific variables derived from information in the main text. For specific situations, better values — if available — may be substituted for site/soil/scenario-related default values. Contaminant-specific values for required variables are included in Table B-6. The emission model provides an output of Q_{av} = time-averaged source strength, expressed in units of mg/d.

At scenario time zero, the contaminant (agent) starts to diffuse upward through the initially uncontaminated soil layer. It follows a tortuous path, continuously partitioning between the solid phase (mainly soil organic matter, though there is some sorption to soil minerals), pore water, and soil air. The following expressions are used to calculate Q_{av} (where default values are inserted as appropriate):

$$D_{ei} = (K_H \times D_a \times \epsilon^{10/3})/(\theta + \epsilon)^2 = (K_H \times D_a \times 0.03802/0.16)$$
$$= 0.2376 \times K_H \times D_a$$

$$K_{da} = K_d + \epsilon/\rho = K_d + (0.375/1.4) = K_d + 0.268$$

$$K_{dj} = (\rho \times K_{da}) + \theta + (\epsilon\ K_H) = (1.4 \times K_{da}) + 0.025 + (0.375\ K_H)$$

and

$$Q_{av} = (2{,}000\ A\ C_a\ D_{ei})/\{K_{da}\ (d_o + [d_o^2 + 2\ D_{ei}\ t/K_{dj}]^{1/2})\}$$
$$= (2 \times 10^7\ D_{ei})/\{K_{da}\ (1 + [1 + 180\ D_{ei}/K_{dj}]^{1/2})\}$$

Table B-5. Factors in the Time-Averaged Flux Analysis

Symbol	Definition	Value
	1. *Site/Soil/Scenario-Related Default Values*	
A	Assumed area of contaminated soil parcel (m^2)	10,000
d_o	Initial depth of top of contaminated soil layer (m)	1
h_o	Initial depth of bottom of contaminated soil layer (m)	3
C_a	Initial agent concentration (dry soil) (mg/kg)	1.0
t	*Emission duration time (days)*	90
ϵ	Air-filled soil void fraction (dimensionless)	0.375
θ	Water-filled soil void fraction (dimensionless)	0.025
ρ	Bulk density of undisturbed soil (kg/L)	1.40
f_{oc}	Fraction of organic carbon in soil (dimensionless) (used only to determine K_d)	0.02
T	*Prevailing temperature (degrees Kelvin)* (used only to determine D_a and K_h)	298
	2. Contaminant-Specific Values	
D_a	Diffusivity of contaminant in air (m^2/d) (Value = 8.64 x D_a expressed in cm^2/s.)	
K_H	Henry's Law Constant for contaminant (dimensionless) (can be obtained by dividing Henry's Law constant in atm-m^3/mol by 8.2 x 10^{-5} x T)	
K_{oc}	Partition coefficient for contaminant between soil organic carbon and water, (mg/kg organic carbon) ÷ (mg/L) [in L/kg]	
K_d	Partition coefficient for contaminant between soil and water = K_{oc} x f_{oc}, (mg/kg) ÷ (mg/L) [in L/kg]	

Table B-6. Contaminant-Specific Values and Derived 90-Day Average Flux Rates for a Hypothetical Scenario

Factor[a]	GB	VX	HD
D_a, m^2/d	0.68	0.49	0.63
K_{oc}	2.8	15.1	100
K_d	0.056	0.30	2.0
K_H	1.62×10^{-5}	2.92×10^{-7}	8.94×10^{-4}
Q_{av}, mg/d	80	0.6	589

a. D_a, K_{oc}, and K_H are derived from tables in the main text.

Although h_o does not appear in the foregoing calculations, it is used in determining the time, t_{dry}, to exhaustion of the contaminant (i.e., when emission stops):

$$t_{dry} = [K_{dj} (h_o^2 - d_o^2)]/[2 D_{ei}]$$

If $t > t_{dry}$, then $Q_{av} = [A \times (h_o - d_o) \times C_a \times \rho \times 10^3]/t$
$= 2.8 \times 10^7/t$, mg/d

Calculations for mustard (HD) average emissions are provided as an example:

$$D_{ei} = 0.2376 \times K_H \times D_a = 0.2376 \times 0.000894 \times 0.63$$
$$= 0.0001338$$

$$K_{da} = K_d + 0.268 = 2 + 0.268 = 2.268$$

$$K_d = (1.4 \times K_{da}) + 0.025 + (0.375\ K_H)$$
$$= (1.4 \times 2.268) + 0.025 + (0.375 \times 8.94 \times 10^{-4})$$
$$= 3.1752 + 0.025 + 0.0003 = 3.201$$

$$Q_{av} = (2 \times 10^7\ D_{ei})/\{K_{da}\ (1 + [1 + 180\ D_{ei}/K_{dj}]^{1/2})\}$$
$$= (2 \times 10^7 \times 0.0001338)/\{2.268\ (1 + [1 + 180 \times 0.0001338/3.201]^{1/2})\}$$
$$= (2676)/(4.545) = 589 \text{ mg/d}$$

Under the assumed conditions, t_{dry} is much larger than t. Note that the value of Q_{av} increases with decreasing d_o.

For a worst-case continuation of the foregoing scenario, assume that the wind is blowing unidirectionally towards a human receptor situated at a short distance downwind of the soil repository. The wind velocity is

4 m/s (roughly 10 mph), blowing across a 100-m edge of the repository (which measures 100 x 100 m); the contaminant is distributed to a height of 2 m. Thus, on average, the volume filled by the contaminant is

$$4 \text{ m/s} \times 86{,}400 \text{ s/d} \times 2 \text{ m} / 100 \text{ m} = 69{,}120{,}000 \text{ m}^3/\text{d}.$$

The average exposure concentration is therefore

$$(589 \text{ mg/d})/(6.9 \times 10^7 \text{ m}^3/\text{d}) = 8.5 \times 10^{-6} \text{ mg/d or } 0.0085 \text{ µg/m}^3.$$

It must be emphasized that empirical evidence, as well as the measured reactivity of the agents of concern with water, would suggest that the above calculations grossly exaggerate potential exposures.

B-6.0 REFERENCES

Bell, E.V., G.M. Bennett, and A.L. Hock, 1927, *Decomposition of Some Halogenated Sulphides, and the Nature of the "Polymeric" Ethylene Sulphides*, J. Chem. Soc., 1803-1809.

Berkowitz, J.B., 1982, *Literature Review - Problem Definition Studies on Selected Chemicals. Final Report. Volume IV. Site Specific Evaluation of Selected Organic Pollutants at Rocky Mountain Arsenal as of 1979*, Contract No. DAMD17-77-C-7037 with U.S. Army Medical Research and Development Command, Arthur D. Little, Inc., Cambridge, MA, March.

Berkowitz, J.B., M.M. Goyer, J.C. Harris, W.J. Lyman, R.A. Horne, L.H. Nelken, J.E. Harrison, and D.H. Rosenblatt, 1978, *Literature Review - Problem Definition Studies on Selected Chemicals. Final Report. Volume II. Chemistry, Toxicology and Potential Environmental Effects of Selected Organic Pollutants*, Contract No. DAMD17-77-C-7037 with U.S. Army Medical Research and Development Command, Arthur D. Little, Inc., Cambridge, MA, June.

Bodek, I., W.J. Lyman, W.F. Reehl, and D.H. Rosenblatt, 1988, *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods*, Pergamon Press, New York.

Committee on Alternative Demilitarization Technologies, 1993, *Alternative Technologies for the Destruction of Chemical Agents and Munitions*, Board on Army Science and Technology, Commission on Engineering and Technical Systems, National Research Council, Washington, DC.

Demek, M., and J. Epstein, 1959, *Project Little Seven Studies. III. Further Studies on the Behavior of VX in Soil*, CWLR 2301, Chemical Corps Research and Development Command, Army Chemical Center, MD (as cited by Small, 1983).

Epstein, J., M. Demek, B.L. Harrison, and J. Kolmerton, 1959, *Project Little Seven Studies. II. Studies on the Behavior of VX in Soils*, CWLR 2291, Chemical Corps Research and Development Command, Army Chemical Center, MD (as cited by Small 1983).

Epstein, J., J.J. Callahan, and V.E. Bauer, 1974, *The Kinetics and Mechanisms of Hydrolysis of Phosphonothiolates in Dilute Aqueous Solution*, Phosphorus, *4*:157-163.

Epstein, J., 1970, *Rate of Decomposition of GB in Seawater*, Science, *170*:1396-1398.

Griffiths, T.A., M.J. Houle, V. Wallace, and F.D. Bagley, 1979, *Extraction and Analysis of Soil Samples from V-Grid at Dugway Proving Ground*, Letter Report DPG-I-135A, Dugway Proving Ground, UT (as cited by Small 1984).

Harvey, S.P, J.J. DeFrank, J.J. Height, C.M. Kutchey, W.T. Beaudry, L.L. Szafraniec, J.J. Valdes, and A.M. Chakrabarty, 1992, "Biodegradation of Mustard," in Reeves, P.J., ed., *Proceedings of the 1990 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research, 13-16 November 1990*, CRDEC-SP-034, U.S. Army Chemical Research, Development & Engineering Center, Aberdeen Proving Ground, MD, pp. 727-734.

Howard, P.H., 1990, *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*, Lewis Publishers, Chelsea, MI.

Kaaijk, J., and C. Frijlink, 1977, *Degradation of S-2-Diisopropylaminoethyl O-Ethyl Methylphosphonothioate in Soil. Sulphur-Containing Products*, Pestic. Sci., *8*:510-514 (as cited by Small 1983).

Kingery, A.F., and H.E. Allen, 1993, *Extraction and Chromatographic Development of Selected Organophosphorus Compounds from Soil and Aqueous Media*, Final Report, prepared for the U.S. Army Environmental Center under Contract No. DAAL03-86-D-0001 by the University of Delaware, Newark, DE, January.

Kingery, A.F., and H.E. Allen, 1994, *Environmental Fate of Alkyl Methylphosphonates Arising from Chemical Surety Material (CSM) and Potential Non-CSM Sources in Soil and Aqueous Media*, Final Report, prepared for the U.S. Army Environmental Center under Contract No. DAAL03-86-D-0001 by the University of Delaware, Newark, DE, March.

Kingery, A.F., and H.E. Allen, 1995, *The Environmental Fate of Organophosphorus Nerve Agents*, Toxicol. Env. Chem., *47*:155-184.

Larsson, L., 1957, *The Alkaline Hydrolysis of Isopropoxy-Methyl-Phosphonyl Fluoride (Sarin) and Some Analogues*, Acta Chem. Scand., *11*:1131-1142.

MacNaughton, M.G., and J.H. Brewer, 1994, *Environmental Chemistry and Fate of Chemical Warfare Agents*, Final Report, SwRI Project 01-5864, Southwest Research Institute, San Antonio TX, March.

Major, M.A., 1990, U.S. Army Biomedical Research and Development Laboratory, Ft. Detrick, MD, Miscibility of DIMP with water, personal communication to D.H. Rosenblatt, December 4.

Nemeth, G., 1989, *RCRA Facility Assessment Report - Edgewood Area - Aberdeen Proving Ground, Maryland No. 39-26-0490-90*, Waste Disposal Engineering Division, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD, November.

Office of Remedial Response, 1988, *Superfund Exposure Assessment Manual, OSWER Directive 9285.5-1, EPA/540/1-88/001*, U.S. Environmental Protection Agency, Washington, DC, April.

Ogston, A.G., E.R. Holiday, J. St. L. Philpot, and L.A. Stocken, 1948, *The Replacement Reactions of 6,6'-Dichlorodiethyl Sulphide and of Some Analogues in Aqueous Solution: The Isolation of 6-Chloro-6'-Hydroxy Diethyl Sulphide*, Trans. Faraday Soc., *44*:45-52.

Puzderliski, A., 1980, *Persistence of Drops of Sarin and Yperite in Soil*, Naueno-Technicki Pregled, *30*:18-23. (Translation from the Serbo-Croation, AD A124201) (as cited by Small 1984).

Roberts, W.C., and W.R. Hartley, 1992, *Drinking Water Health Advisory: Munitions*, Lewis Publishers, Boca Raton, FL.

Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul, and D.R. Cogley, eds., 1975, *Problem Definition Studies on Potential Environmental Pollutants. II. Physical, Chemical, Toxicological, and Biological Properties of 16 Substances*, Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD. AD A030428.

Sass, S., T.N. Zenk, and R.A Hilliard, 1953, *Stability of Agents in Soils (GA, GB, GF, EA1211, Paraoxon, EA 1370)*, CRLR 247, Chemical Corps Chemical and Radiological Laboratories, Army Chemical Center, MD.

Small, M.J., 1984, *Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate*, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, Technical Report 8304, June. AD-A149515.

Small, M.J.,1993, *The Pollutant Hazard Assessment System, Version 3: Documentation and Users Manual*, Technical Report 9302, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD, May.

Small, M.J., 1983, *Soil Detection Limits for Potential Chemical Warfare-Related Contaminants at Fort McClellan Alabama*, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, Technical Report 8208, May. AD-B077091L.

Szafraniec, L.J., L.L. Szafraniec, W.T. Beaudry, and J.R. Ward, 1990, *On the Stoichiometry of Phosphonothiolate Ester Hydrolysis*, CRDEC-TR-212, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, July.

Szafraniec, L.L., W.T. Beaudry, and Y.-C. Yang, 1993, *Hydrolysis of VX and S-2-(Diisopropylamino)ethyl Methylphosphonothioic Acid (EA2192) in Super-Alkaline Solution*, Proceedings, 1992 ERDEC Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 17-20, 1992.

USATECOM, undated, *Environmental Impact Statement for the Study of the Fate of Agent and Residues in Vegetation and Soil*, USATECOM Project 5-CO-483-000-015, Deseret Test Center, Fort Douglas, UT.

Verweij, A., and H.L. Boter, 1976, *Degradation of S-2-Diisopropylaminoethyl O-Ethyl Methylphosphonothioate in Soil. Phosphorus-Containing Products*, Pestic. Sci., 7:355-362 (as cited by Small 1983).

Weast, R.C., 1979, *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, FL.

Williams, A. and I.T. Ibrahim, 1981, *A New Mechanism Involving Cyclic Tautomers for the Reaction with Nucleophiles of the Water-Soluble Peptide Coupling Agent 1-Ethyl-3-(3-(dimethylaminopropyl) carbodiimide (EDC)*, J. Am. Chem. Soc., *103*: 7090-7095.

Yang, Y-C., L.L. Szafraniec, W.T. Beaudry, and J.R. Ward, 1987, *Sulfonium Chlorides Derived from 2-Chloroethyl Sulfides. I. Formation and Magnetic Resonance Identification in Water*, CRDEC Technical Report TR-88008, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, October.

Yang, Y-C., L.L. Szafraniec, W.T. Beaudry, and D.K. Rohrbaugh, 1990, *Oxidative Detoxification of Phosphonothiolates*, J. Am. Chem. Soc., *112*:6621-6627.

APPENDIX C

ABSORPTION AND DESORPTION OF CHEMICAL AGENTS ON POLYMERIC MATERIALS

C-1.0 INTRODUCTION

This Appendix seeks to provide an understanding of the absorption and desorption of liquid chemical agents in polymeric substrate materials. Such phenomena relate to the ability of decontaminants applied to substrate surfaces to reactively decompose and remove the agents. The polymeric substrate materials of special interest are:

Alkyd paints (on metal)
Polyurethane paints (on metal)
Butyl rubber
Neoprene rubber
Polystyrene
Polymethyl methacrylate
Chemically protective fabric (materials not specified)

Unfortunately, no direct evidence concerning the absorption or desorption of the chemical agents with these specific substances has been located in the open (peer-reviewed journal) literature, but a moderate about of relevant information is available in military documents.

Substrates are usually tested with liquid agent contamination densities of up to 10 g/m^2 nominal surface density (Southern Research Institute 1992). This density should be put into common perspective. The application of one-coat wall paint corresponds to an approximate surface density of 1 gallon per 300 ft^2. If one assumes that the mass density of paint is 1 g/cm^3, after conversions of weight and area, the paint application corresponds to a surface density of 136 g/m^2, about 14 times that planned for agent. Moreover, if the density of agent is about 1.1 g/cm^3, a 10 g/m^2 uniform surface density would have a depth of 0.009 mm. In comparison, the average plastic trashbag is about 0.8 mil or 0.020 mm, approximately twice as thick. Because agent is applied as discrete droplets, the initial agent film on a substrate is likely to be rather uneven.

C-2.0 ABSORPTION INTO POLYMERIC SUBSTRATE MATERIALS

In this discussion, polymeric substrate materials are assumed to be nonporous. For a liquid substance or permeant to be absorbed into a polymeric material, it must "dissolve" in the polymer and then diffuse through the polymeric structure (Perkins and Tippit 1985). The absorption process is usually studied in terms of the kinetics of reaching equilibrium under isothermal conditions. Two parameters are involved: the solubility of the permeant in the polymer at equilibrium and the diffusion coefficient (characteristic of the kinetics of permeant movement into the polymer).

The question of polymer-liquid solubility has been extensively studied, and the extent of solubility can be qualitatively predicted by considering the solubility parameters (δ) for the polymer and liquid. This parameter is defined as the square root of the ratio of molar energy of evaporation to molar volume (Grulke 1989). This parameter is cited in units of either $(cal/cm^3)^{0.5}$ or $(MPa)^{0.5}$; here, $(cal/cm^3)^{0.5}$ will be assumed unless otherwise specified.

For nonpolar liquids and vapors, and in the absence of hydrogen bonding, the Hildebrand-Scatchard regular solution theory has been used as a starting point to determining if a noncrystalline polymer dissolves in a liquid (Blanks and Prausnitz 1964). The theory involves computing the free energy of mixing, in which the solubility parameters for the system liquid and polymer appear. If these parameters differ by less than 1.7 to 2.0 (Billmeyer 1971), polymer dissolution in liquid may be expected.

Hansen (1969) extended this theory to the problem of permeability of solvent in polymer. He postulated that the solubility parameter could be treated as the vector sum of four components, of which three were considered most important: those of dispersive forces, permanent dipoles, and hydrogen-bonding attributes. These parameters have been measured for hundreds of solvent compounds and many polymeric materials and are tabulated in standard references (Barton 1983, 1990; Grulke 1989) and in computer databases (Shuely 1993). For convenience, parameters collected for compounds mentioned in this appendix are listed in Table C-1. Alkyd paint solubility parameters are also available.

Table C-1. Solubility Parameter Data for Chemical Agents, Solvents, and Polymeric Materials

Permeant	δ^a	Source	Polymer	δ^a	Source
GB	9.0 [b]	Pfau et al. 1987	Polymethyl methacrylate	9.1,5.1,3.7,11.1	Barton 1983
GD	8.6 [b]	Pfau et al. 1987	Polystyrene	10.4,2.8,1.3,10.6	Barton 1983
VX	8.5 [b]	Pfau et al. 1987	Neoprene	9.5,1.5,1.3,9.7	Barton 1990
HD	9.5, 3.8, 2.4, 10.5[c]	Shuely and McNeely, 1992	Butyl Rubber	7.8,1.1,1.6,8.0	Barton 1990
Toluene	8.8,0.7,1.0,8.9[c]	Barton 1983	Polypropylene	8.2 [b]	Michaels et al. 1968
Methylcyclo-hexane	7.8,0.0,0.5,7.8 [c]	Barton 1983	Styrene-Butadiene Rubber	8.6,1.7,1.3,8.9	Barton 1983
n-Heptane	7.5,0.0,0.0,7.5 [c]	Barton 1983	Polyethylene	8.6,0.0,0.0,8.6	Barton 1983
Methyl acetate	7.5,3.5,3.7,9.1[c]	Barton 1990	PVC	8.9,3.7,2.1,9.9	Barton 1983

a Values given in order: dispersive, polar, H-bonding, and total.
b No component values available from reference.
c Data in $(MPa)^{1/2}$, converted by the author [1 $(Mpa)^{1/2}$ = 2.046 $(cal/cm^3)^{1/2}$].

Shuely (1993) presents a detailed procedure to predict if a chemical agent is soluble in a given polymer. A solubility parameter database with selected polymers was assembled for liquids known to be soluble or insoluble. A three-dimensional surface (the dimensions representing dispersion, polarity, and hydrogen-bonding aspects of the solubility parameter), which encloses the polymer's solubility space, can be constructed. To assess a candidate liquid for permeability, the liquid's location in solubility parameter space is determined to be inside or outside the polymer's solubility space. The theory does not suffice to estimate saturation solubility for agent. Mangaraj et al. (1987) present a method to estimate phosphonofluoridate agent solubility and diffusion coefficients in polymers based on experimental results with several simulant liquids. Perkins and Tippit (1985) indicate some progress in correlating permeation rate and breakthrough times to the vector distance from the "center" of the polymer's solubility space to the permeant.

C-2.1 Methods and Models

When a solid is immersed in a liquid or vapor containing an absorbable substance, the relationship between the amount of the substance that sorbs into the solid and the concentration of the substance in the liquid or vapor phase at a fixed temperature is called an absorption isotherm. Absorption isotherms can be measured with permeant in the liquid or vapor state. Generally, thin films of polymer are used, although for vapor experiments, powdered materials may be employed (Berens 1985). Liquid absorption isotherms can be developed by immersing the polymer sample in liquid. At selected time intervals, the sample is removed from the liquid, blotted dry, and weighed. The vapor absorption isotherm tests have been performed with the sample attached to a calibrated quartz spring in a test cell, which is filled with vapor permeant that is maintained at a preselected pressure. The increase of polymer weight due to absorption is indicated by the elongation of the spring, which can be followed visually. More recently, gravimetric devices such as recording microbalances have been developed to follow the weight gain with time.

The test results are expressed as a curve of weight gain vs. elapsed time. The ratio of weight gain to polymer sample weight approaches an asymptotic value, which is the saturation solubility for the permeant. The saturation solubility of a permeant in a given polymer depends on whether the permeant is applied as a liquid or vapor, on the temperature, and — for vapor contact — on the vapor pressure. Solubility is also a function of polymer structure. Crystalline nonpolar polymers and cross-linked polymers resist the permeation of otherwise soluble nonpolar permeants. For example, in work by Long (1965), solubility predictions with polymers of differing crystalline content were obtained by adjusting for the crystalline content.

The saturation solubilities for permeant liquid and saturated vapor are expected to be equal due to thermodynamic considerations. However, the solubility at lower permeant activities may be considerably lower than expected from Henry's Law. Berens (1985) experimentally determined absorption isotherms for several permeants in polyvinyl chloride (PVC), either at saturated conditions or with unsaturated vapor or diluted liquid (in nondiffusing solvent). As an example, the weight gain of PVC in contact with liquid toluene (activity = 1) was about 55% of initial polymer sample weight. At an activity of 0.75 (either toluene vapor at 75% of saturated vapor pressure or a toluene-polyethylene glycol solution that produces the same pressure), the weight gain was only 16%; at an activity of 0.5, the weight gain was just 8%. Berens (1985) explains the relation in terms of the Flory-Huggins equation: $\ln (P/Po) = \ln(V1) + V2 + \chi V2^2$. In this equation, P/Po is the activity, V1 is the volume fraction of permeant in polymer at equilibrium conditions, V2 is the volume fraction of polymer at equilibrium conditions, and χ is the Flory interaction parameter, which in this application is a curve-fitting parameter. Usually, χ provides a semi-qualitative criterion to predict if a solvent softens a polymer or causes polymer swelling and is a function of both the solvent and polymer. Values of χ for selected systems are also tabulated (Barton 1983; Grulke 1989).

Several models, based on mathematical solutions to the diffusion equation, can be used for data analysis. The simplest model is one-dimensional diffusion, in which the diffusion coefficient of the permeant within the polymer is independent of permeant concentration. In experiments that fit this model, the initial part of the curve exhibits a linear uptake-$(\text{time})^{1/2}$ behavior. A pseudosaturation time is determined by extrapolation of the line (uptake vs. $[\text{time}]^{1/2}$) to the estimated saturation solubility. If half this time is called $t_{1/2}$sat, the diffusion coefficient is computed as $D = 0.0492\ L^2 / t_{1/2}\text{sat}$, where L is the thickness of the polymer parallel to the direction of diffusion. In Naylor (1989), this is called Case I sorption. Case I sorption is often encountered with permeants into polymeric materials above the glass transition point (Crank 1956).

A more complicated situation arises if the diffusion coefficient is a function of permeant concentration within the polymer. This situation was encountered by Long (1965), who studied the permeation of toluene, n-heptane, and methylcyclohexane in polypropylene, and by Berens (1985), whose work is described above. In this case, the weight gain–time relation tends to be more linear. The condition of a linear weight gain–time relation has been called Case II sorption (Naylor 1989).

Long (1965) estimated a zero-concentration diffusion coefficient, D_o, for the model $D=D_o e^{aC}$, where

D is the diffusion coefficient for a specific concentration of permeant in polymer,
C is the point concentration, and
a is a constant for a given temperature and polymer-solvent system.

D_o was determined from data obtained by desorbing a polymer sample that had been equilibrated with the saturated vapor of a permeant. The polymer sample of thickness L was suspended on a quartz spring in an enclosed case. Vacuum was applied to an outlet, and as desorption occurred, the polymer weight (as measured from the elongation of the spring) was obtained. After an extended time period, the slope of the ln (weight) vs time curve should approach $\pi^2 D_o/L^2$. At room temperature, the diffusion coefficient of liquid toluene was estimated as $3x10^{-6}$ cm^2/sec, while D_o was computed to be $1.5x10^{-9}$ cm^2/sec.

One major difference between the two models is the concentration profile of permeant in the polymer. For Case I sorption, the profile has been determined and presented in dimensionless figures (see Crank 1956) (Section C-3). The polymer is saturated just inside the surface, and the concentration decreases monotonically towards zero at greater depths. In Case II sorption, the profile approaches a "step" function (depending upon the model relation for D and the fit parameter). The permeant diffuses into the polymer as a "front," and, at any time in the process, the transition from saturated to near-zero concentration in polymer occurs over a short thickness interval. Experimental observations show that the nearly saturated portion of the polymer will swell considerably, while the nearly dry portion has normal dimensions. Berens (1985) observes that at low activity levels, absorption into PVC was described by the Case I sorption model, but as the activity increased, the isotherms tended towards Case II sorption behavior. For example, Case I sorption isotherms were determined for toluene at activities of 0.75 or lower.

In short, under some conditions an agent may show a gradually decreasing concentration profile as it penetrates a polymer substrate, the forward edge of the migrating agent.

C-2.2 Diffusion of Chemical Agents

Pfau et al. (1987) studied the absorption of saturated vapors of the chemical agents GB, GD, VX, and HD in low-density polyethylene (LDPE) and styrene-butadiene rubber (SBR). Their data are reviewed here, and the *intake per m^2 area is estimated for a 1-h (3,600-s) exposure to illustrate the extent of permeation of liquid at* a 10 g/m^2 surface density. The results calculated from these data appear in Table C-2.

Table C-2. Agent Permeation Estimated for 1-h Exposure to Saturated Vapor, Based on Data of Pfau, et al. (1987)

Agent/Polymer	GB/LDPE	GB/SBR	GD/LDPE	GD/SBR	HD/LDPE	VX/LDPE
D (cm^2/s)	$1.3x10^{-8}$	$4.9x10^{-8}$	$1.3x10^{-9}$	$8.7x10^{-9}$	$3.1x10^{-9}$(a)	$3.8x10^{-9}$(a)
Solubility (g/g)	0.003	0.12	0.016	0.23	0.022(a)	0. 062(a)
$t_{1/2}$sat (s)	39,200	29,800	500,000	113,000	180,000	146,000
L (cm)	0.10	0.17	0.11	0.14	0.11(b)	0.11(b)
fraction, 1 h	0.214	0.246	0.06	0.126	0.1	0.011
Agent sorbed (g), in 1 h	0.65	51	1.1	41	2.4	0.74

[a] Estimated by the author.
[b] Assumed thickness.

GB and GD diffusion coefficients and solubility values are presented in Table 2 of the report by Pfau et al. (1987). Because polymer thickness data are not provided, the "Case I" equation discussed above is used to back-calculate the thickness L. The term "fraction, 1 h" is the ratio of $(3,600)^{1/2}/(tsat)^{1/2}$ and indicates the extent of total absorption that is attained in 1 h. (Note that tsat = 2 x $t_{½}$ sat.) The weight of agent sorbed in one hour is the product: (saturation solubility) x L x 10,000 x (fraction, 1 h). The polymer is assumed to have unit density. For HD and VX, absorption curves are presented by Pfau et al. (1987), but the solubility and the diffusion coefficient are not estimated. Estimates of these factors and saturation time in Table C-2 were made by the authors of the present document. The LDPE test material for HD and VX experiments was assumed to be 0.11 cm thick.

The results in Table C-2 should be considered tentative because agent vapor-polymer data have been applied to an agent liquid-polymer scenario. The present authors consider this a valid approach for two reasons. First, Long (1965) indicates that, for liquids with low permeation rates, the liquid and vapor permeation rates should be equal. Second, liquid agent does not cover the entire surface, and the areas unexposed to liquid would be subject to vapor penetration from evaporating liquid. The analysis does suggest that a significant amount of agent could permeate into either SBR or LDPE in 1 h.

It can be seen that the capacity of substrate polymers to absorb agents varies widely.

C-3.0 DESORPTION

Once an external supply of permeant is removed from a polymeric substance that has absorbed a permeant, desorption can take place. The transport mechanism of permeant away from the surface plays the major role in controlling the rate of desorption, as does the dependence of the diffusion coefficient on concentration.

The simplest situation is that of a polymer fully saturated with permeant, where Case I sorption applies, that is suddenly exposed to an external environment where the exiting vapors are instantly dispersed. A practical example would be agent-saturated polymer immersed in a decontamination liquid that is not soluble in the polymer. In terms of the Fickian diffusion equation, $\partial C/\partial t = - D \partial^2 C/\partial x^2$ (where x is the length dimension, the boundary conditions prevailing during absorption are simply reversed. Thus, desorption should proceed, at least in theory, as did absorption, with the same mass of permeant removed in the same time as it took for that mass to absorb. In practice, there is hysteresis (a lag of effect when the direction of action is reversed), with the desorption rate somewhat lower than that of absorption. Experimental observations to this effect are discussed by Crank and Park (1968); in one example, that of methyl acetate in polymethyl acrylate, the slope of the mass desorbed-$(time)^{1/2}$ line was 0.8 that of the absorption line.

For a partially saturated polymer, the situation is more complex; the concentration profile of permeant in polymer at the start of desorption is not uniform. Crank (1956) provides dimensionless profiles for contours of $4Dt/L^2$. The HD/LDPE data from Table C-2 give a contour value of 0.0037. The nearest exemplar profile, for 0.005 (Crank 1956), indicates the following:

Distance inside Surface, cm	Percent Saturation
0.0	100
0.006	30
0.011	4
0.016	0.4

As HD diffuses from the polymer, the driving gradient will decrease rapidly because the interior layers are not saturated. Moreover, there is still a gradient inwards, so HD will continue to penetrate the polymer to greater depths. In this case, the desorption rate should be considerably below the rate for a fully saturated polymer sample.

Crank (1956) also presents dimensionless desorption curves for the case in which permeant exiting the surface is subject to less-than-instantaneous dispersion according to the relation: $-D\,\partial C/\partial x = \alpha(Co-Cs)$, where Cs is the permeant concentration just within the polymer and Co is the ambient external concentration of permeant. The parameter α has units of length/time. If the external environment is permeant-free air, α may be looked upon as an exchange coefficient.

If the diffusion coefficient is concentration dependent, the rate of desorption is less than that of the absorption that preceded it. Crank (1956) has illustrative curves for the exponential model, $D = D_o\, e^{\alpha C}$, discussed in Section C-2.1, as well as for other diffusion-concentration models.

In summary, diffusion of an agent out of a polymeric substrate may require considerably more time than its diffusion into the substrate.

C-4.0 IMPLICATIONS

The models described above are useful guides for the design of experiments to determine quantitative absorption relationships between the agents of concern and the organic substrates of special interest. The solubility parameters in Table C-1 provide information on polymethyl methacrylate, polystyrene, neoprene rubber, butyl rubber, and the four agents. The nonpolar Hildebrand-Scatchard theory, as cited by Billmeyer (1971) would indicate that the agents are soluble in these polymers to an appreciable extent [$|\delta_{agent} - \delta_{polymer}| < 2$]. A better assessment can be made when the dispersive, polar, and hydrogen bonding components of agent solubility parameters are obtained. The work by Pfau et al. (1987) indicates that the agents will diffuse into SBR, a substance similar in solubility parameter characteristics to the other rubbers of special interest. The desorption from such materials, even when the materials are treated with decontaminants, may not suffice to remove all diffused (imbibed) agent in the time frame of concern.

It is quite likely that time constraints will render the complete decontamination of sorbed agents from thick layers of polymer highly impractical.

C-5.0 REFERENCES

Barton, A.F.M., 1983, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Inc., Boca Raton, FL.

Barton, A.F.M., 1990, *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Inc, Boca Raton, FL.

Berens, A.R., 1985, "Prediction of Organic Chemical Permeation through PVC Pipe," J. Amer. Waterworks Assn., November, p. 57-64.

Billmeyer, F.W., Jr., 1971, *Textbook of Polymer Science*, Wiley Interscience, John Wiley and Sons, New York, NY.

Blanks, R.F., and J.M. Prausnitz, 1964, *Thermodynamics of Polymer Solubility in Polar and Nonpolar Systems*, I&EC Fundamentals *3*(1):1-7.

Crank, J., 1956, *The Mathematics of Diffusion*, Oxford University Press, London, UK.

Crank, J., and G.S. Park, 1968, *Diffusion in Polymers*, Academic Press, New York, NY.

Grulke, E.A., 1989, "Solubility Parameter Values," in J. Brandrup and E.H. Immergut, eds., *Polymer Handbook*, Chapter 7, Third Edition, Wiley Interscience, John Wiley and Sons, New York, NY.

Hansen, C.M., 1969, *The Universality of the Solubility Parameter*, I&EC Prod. Res. Dev. *8*(1):2-11.

Long, R.B., 1965, *Liquid Permeation through Plastic Films*, I&EC Fundamentals *4*(4): 445-451.

Manjaraj, D., J.P. Pfau, M. Luttinger, F. Block, and W.S. Magee, 1987, *An Approach to Estimating the Permeation of Phosphonofluoridates into a High Polymer Matrix Part 1. Development of the Approach*, Polymer Eng. Sci. *27*:1338-1343.

Michaels, A.S., W.R. Veith, and H.H. AlCahay, 1968, *The Solubility Parameter of Polypropylene*, J. Appl. Poly. Sci. *12*:1621-1624.

Naylor, T. deV., 1989, "Permeation Properties," in C. Booth, and C. Price, eds., *Comprehensive Polymer Science, Volume 2, Polymer Properties*, Chapter 20, Pergamon Press, New York, NY.

Perkins, J., and A.D. Tippit, 1985, *Use of Three-Dimensional Solubility Parameters to Predict Glove Permeation*, Am. Ind. Hyg. Assoc. J. *46*(8):455-459.

Pfau, J.P., R.E. Sharpe, D. Manjaraj, J.D. Booton, F. Block, and W.S. Magee, 1987, *An Approach for Estimating the Permeation of Chemical Warfare Agents into a High Polymer Matrix Part II. Verification of the Approach.* CRDEC-CR-87090, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June, DTIC AD-B113662L.

Shuely, W.J., 1993, *Test Methodology for Development of Corrosion Resistant Polymeric Materials: Predictive and Experimental Methods for Chemical Resistance Screening*, 12th Biennial Managing Corrosion with Plastics Symposium, Baltimore, MD, November 1-4.

Shuely, W.J., and J.J. McNeely, 1992, *Material Selection Guide Derived from Material-Chemical Compatibility Database: Feasibility Based on Database and Predictive Model Evaluation*, CRDEC-TR-397, Chemical Research, Development and Engineering Center, Edgewood, MD, September. DTIC AD-A266508.

Southern Research Institute, 1992, *Waste Sampling Test Report*, Final Report, Contract DAAA15-89-D-0004, Task Order No. 11, SRI-APC-92-552-6840-45, Project 6840-45/XXVI, by Southern Research Institute, Birmingham, AL.

Background Document I, Reference 16

Rosenblatt, D.H., et al., 1975, Problem Definition Studies on Potential Environmental Pollutants, Technical Report 7509, U.S. Army Medical Bioengineering Research and Development Center, Fort Detrick, Md.

See Background Document B, Reference 48

Background Document I, Reference 17

Safety Office, 1995, "Material Safety Data Sheet for HQ," U.S. Army Chemical, Research, Development, and Engineering Center, Aberdeen Proving Ground, Md. (June).

See Background Document D, MSDS Sheets

Background Document I, Reference 18

Samuel, J.B., et al., 1983, Physical Properties of Standard Agents, Candidate Agents, and Related Compounds at Several Temperatures (U), Special Publication ARCSL-SP, Chemical Systems Laboratory, Aberdeen Proving Ground, Md. (June).

See Background Document B, Reference 55

EDGEWOOD
RESEARCH, DEVELOPMENT & ENGINEERING CENTER
U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-458

AGENT NEUTRALIZATION STUDY
II: DETOXIFICATION OF HD WITH AQUEOUS BLEACH

John B. Samuel
William T. Beaudry
Dennis K. Rohrbaugh
Linda L. Szafraniec
Ann B. Butrow
Lawrence R. Procell
David C. Sorrick
Yu-Chu Yang

RESEARCH AND TECHNOLOGY DIRECTORATE

January 1998

Aberdeen Proving Ground, MD 21010-5423

AD 554162

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1998 January	Final; May 93 - Aug 93

4. TITLE AND SUBTITLE
Agent Neutralization Study, II: Detoxification of HD with Aqueous Bleach

5. FUNDING NUMBERS
MIPR-M3-07-148

6. AUTHOR(S)
Samuel, John B.; Beaudry, William T.; Rohrbaugh, Dennis K.; Szafraniec, Linda L.; Butrow, Ann B.; Procell, Lawrence R.; Sorrick, David C.; and Yang, Yu-Chu

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
DIR, ERDEC, ATTN: SCBRD-RTC, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDEC-TR-458

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
PMCD, ATTN: SFAE-CD-A, APG, MD 21010-5401

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A series of neutralization studies was conducted by reacting varying amounts of HD with aqueous hypochlorite (OCl^-) solution to evaluate the use of bleach as an alternate means of destroying stockpiles of HD. A small vacuum jacketed glass reactor was used to react CASARM grade HD and one ton container HD sample. One mid-scale reaction with ton container HD was also conducted. Exotherms were observed in each reaction, and the heat of reaction was estimated. Analyses of selected products by NMR and GC/MS are reported. Sodium hydroxide as a stabilizer for the bleach was studied. Reaction products were titrated for active chlorine. Thiodiglycol was reacted with OCl^- for comparison. The stability versus time for bleach solutions at 75 °C is reported.

A large variety of compounds are formed during the oxidation of HD, which proceeds by a complex and inexact stoichiometry. At least 5 moles of OCl^- are required to destroy all of the HD, and significant heat is produced during the reaction. However, the reaction is more controlled and more efficient when caustic is used as a bleach stabilizer. Ton container HD required more OCl^- due to the oxidation of the extra sulfides.

14. SUBJECT TERMS

HD	Hypochlorite	NaOCl	Sulfone	Glass reactor
HTH	Thiodiglycol	Hydrolysis	Sulfoxide	Exotherms
NMR	GC/MS	Stabilizer	NaOH	Neutralization
GC	Oxidation	Bleach	Active chlorine	

15. NUMBER OF PAGES
31

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

PREFACE

The work described in this report was authorized under MIPR No. M3-07-148, Joint U.S. Army Edgewood Research, Development and Engineering Center/Office of the Program Manager for Chemical Demilitarization Chemical Agent Neutralization Study. This work was started in May 1993 and completed in August 1993.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

The authors express their appreciation to Marion A. Casteel, George L. Smith, Phillip C. Rice, Jr., Michael J. Manthei, and Cinderella M. Church, Operations Directorate, ERDEC, for help in conducting the mid-scale reaction at the Chemical Transfer Facility. The authors would also like to thank MAJ Jean Luc Ontivaros, Office of the Program Manager for Chemical Demilitarization, for administrative support.

CONTENTS

FIGURES

TABLES

AGENT NEUTRALIZATION STUDY
II. DETOXIFICATION OF HD WITH AQUEOUS BLEACH

1. INTRODUCTION

This study was undertaken to provide the Office of the Program Manager for Chemical Demilitarization (OPMCD) and the National Research Council's Committee on Alternative Technologies information that would allow assessment of OCl^- oxidation of HD as an alternative to incineration for the destruction of chemical stockpiles. Of particular interest was the minimum amount of OCl^- that is required to destroy HD. Yurow and Davis[1] state that the stoichiometry of the OCl^- oxidation of HD is indefinite due to the many products formed. They then presented a worst case reaction where HD is oxidized completely to CO_2 as follows:

$$(ClCH_2CH_2)_2S + 7Ca(OCl)_2 + 2Ca(OH)_2 \rightarrow CaSO_4 + 8CaCl_2 + 4CO_2 + 6H_2O \quad \text{(Eq. 1)}$$

The stoichiometry of this reaction was used for the Delisting Studies[2] submitted to the State of MD for the laboratory decontamination of HD. Yang et al[3] indicate that the HD sulfoxide is first formed, followed by the sulfone, monovinyl and divinyl sulfoxides and sulfones.

In the current study, mole ratios below the 14/1 ratio OCl^-/HD used in Equation 1 were studied. Small-scale reactions were run at various levels of OCl^- to determine the minimum amount required to destroy all of the HD. The sources of OCl^- were NaOCl from household bleach and $Ca(OCl)_2$ from aqueous solutions of HTH.

To evaluate the feasibility of the reaction for plant use, the quantity of heat generated during the process is also of critical importance. Small-scale reactions were run in a vacuum jacketed glass reactor to minimize heat loss. To evaluate the effect of scale-up on final temperature, one mid-scale reaction was run in addition to the small-scale reactions.

2. EXPERIMENTAL PROCEDURES

2.1 Materials.

Chemical Agent Standard Analytical Reference Material (CASARM) HD Lot HD-U-2325-CTF-N, 97.5 ± 0.2 mole% by FPD, 97.3 mole% by NMR.

Ton container HD, Lot HD-S-2296-CTF-N-1 (NMR (mole %): ~90-93% HD, major impurity, $[ClCH_2CH_2SCH_2]_2$, Q; GC/MS/CI (area %):

89.2% HD; 4.7% Q; 2.4% 1,2-dichloroethane; 1.2% 1,4-dithiane; 1.7% C_6 isomers; 0.4% C_5 isomer; 0.1% HD disulfide; 0.3% other).

HTH, $Ca(OCl)_2$, Lot No. L6B-889A; 67% active chlorine by titration.

Household bleach, 4.3 wt% NaOCl by titration, Lot No. D2139A7, manufactured by James Austin Co., Mars, PA.

NaOH pellets, ACS grade, Lot No. 7708 KBDL, manufactured by Mallinckrodt, Inc., Paris, KY.

Chloroform, reagent grade, Lot No. 519182, manufactured by Baker Chemical Co., Phillipsburg, NJ.

Sodium thiosulfate, ACS grade, Lot No. 7-3EEX, manufactured by City Chemical Co., New York, NY.

Potassium iodide, analyzed reagent, Lot No. 050097, manufactured by J. T. Baker Chemical Co., Phillipsburg, NJ.

Potassium iodate, certified ACS, Lot No. 781821, manufactured by Fisher Scientific Co., Fairlawn, NJ.

Thiodiglycol (TDG), Lot No. 69F-0720, manufactured by Sigma Chemical Co., St. Louis, MO.

Water: The source for small-scale tests was building E3300 distilled water taps. Building E3832 distilled water was used for the mid-scale test.

2.2 Stability of Aqueous HTH and NaOCl Solutions at 75 °C.

Stability studies of 4.3 wt % household bleach and a 10% aqueous solution of HTH were conducted at 75 °C. The samples were prepared in the following manner:

a. Household bleach (200 mL) was placed in a 250 mL Erlenmeyer flask, and the flask was stoppered.

b. HTH (20 g) was placed in a 250 mL Erlenmeyer flask and brought to 200 mL using deionized water. The sample was mixed vigorously to dissolve soluble chemicals.

Both samples were placed in a 75 °C covered water bath and heated without mixing. Flasks were swirled just prior to sampling the solutions. Titrations were conducted under acid conditions using 0.1 N sodium thiosulfate to titrate iodine formed from the oxidation of potassium iodide by active chlorine.

2.3 Reaction Procedures.

2.3.1 Small-Scale Reactions.

Most reactions were run in a small-scale vacuum jacketed glass reactor (figure 1). The reactor had a capacity of approximately 50 mL up to the lower portion of the boat well. Stirring was provided by a magnetic stirring bar at 450 rpm which resulted in a well formed vortex. The temperature was measured using a 1/16" diameter type T, stainless steel sheathed copper-constantan thermocouple connected through an electronic icepoint reference to a strip chart recorder set at 10 mv full scale and a chart speed of 1 cm/min. Thermocouples were checked using boiling water and an ice bath. The reported temperatures should be accurate to within 1 °C except during periods of rapid temperature change due to thermocouple lag. A vent tube was provided to allow permanent gases to escape and to collect some of the condensable vapor. The boat was used to add the HTH several minutes prior to the reaction. The stirring was stopped, and the stopper with vent tube and thermocouple were removed so that HD could be added below the surface of the liquid. A vacuum was pulled on the reactor jacket prior to and during the reaction. Time zero was taken when the stirring was started. One reaction was run with a modified setup to allow an Orion-Ross type 8104 combination pH electrode to be placed in the reactor. An Orion Research Model 811 pH meter connected to a strip chart recorder was used to follow the reaction. The meter was calibrated with pH 4.00 and 10.00 standards.

Elevated starting temperatures were achieved by heating the glass reactor containing the weighed amount of water to the desired starting temperature. Once the desired temperature was achieved, the HTH was added using the boat and mixed for ~5 min prior to adding the agent.

Several small-scale reactions were run in 50 mL Erlenmeyer flasks fitted with a thermocouple. HD was added to the bleach solution while stirring was provided by a magnetic stirring bar.

2.3.2 Mid-Scale Reaction Study.

One mid-scale reaction was run by personnel at the Chemical Transfer Facility (CTF), Operations Directorate, ERDEC, using 46.7 mL (60 g) of ton container HD reacted with 200 g HTH in 2000 mL water stabilized with 66.7 g NaOH (2.58 wt% HD, 8.5 wt% of 67% active HTH, and 2.87 wt% NaOH). The reactor consisted of a 3000 mL roundbottom distillation flask with three standard necks and a thermometer port. A motor driven stirring paddle was inserted through the first neck, and a vented reflux column was fitted to the second neck. The third neck was stoppered and was used for the agent addition, sampling and the momentary insertion

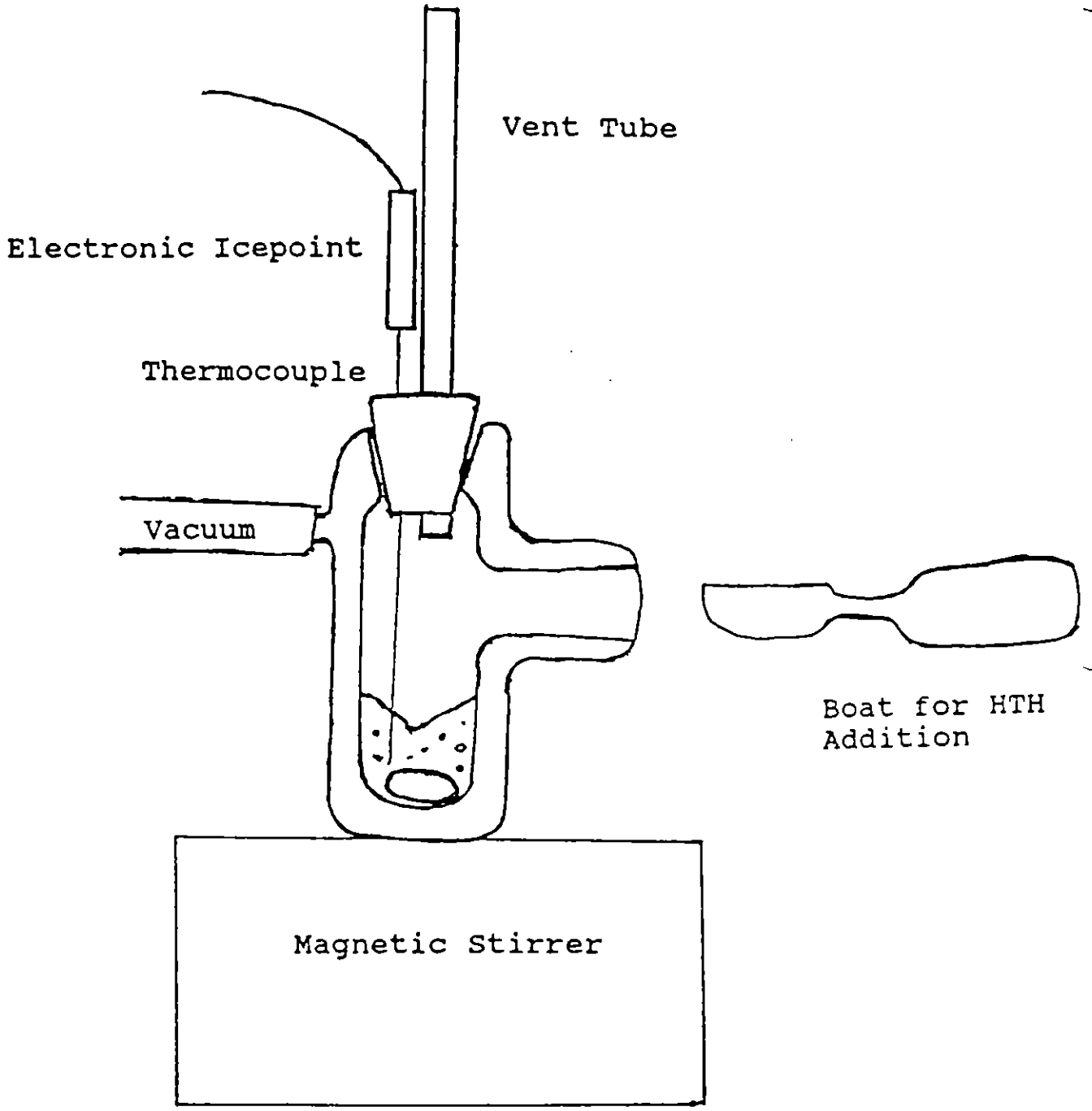


Figure 1. Small-Scale Glass Reactor.

of a pH probe. A 1/16" diameter type T copper-constantan shielded thermocouple was fitted through a small rubber stopper and inserted through the thermometer port. The HTH was dissolved as much as possible, then NaOH added and dissolved. The decon solution was allowed to cool to 32 °C then the stirring was stopped. Using a 50 mL syringe with a 13 gauge needle, the agent was then added below the surface of the decon solution. An identical syringe and needle were calibrated using distilled water, which allowed the needle void to be included in the volume delivered. Once the agent addition was completed, stirring was resumed, and the time was taken as T_0. Instrumentation for temperature and pH measurements was identical to that described in the above section on the small-scale reactor.

2.4 Analytical Procedures.

2.4.1 Gas Chromatography/Mass Spectrometry (GC/MS) Analysis.

Samples were analyzed on a Finnigan Model 5100 GC/MS equipped with a 15 m x 0.25 mm (i.d.) J+W DG-1701 capillary column. Injector temperature was 210 °C, and the GC/MS interface temperature was 230 °C. Samples were analyzed in the chemical ionization (CI) mode using methane (0.5 Torr) as the CI reagent gas. The ion source temperature was 100 °C, and the oven temperature was programmed from 60 to 270 °C at 10 °C/min. The mass range was scanned from 60-500 amu at 1 scan/sec. Spectral identifications were obtained by comparison to spectra in existing user libraries or on the basis of CI fragmentation patterns.

For derivatization, 0.2 mL of sample was evaporated to dryness with gentle heating under a stream of dry argon. The residue was dissolved in approximately 0.2 mL of bis-(trimethylsilyl) trifluoracetamide (BSTFA) and heated to 60 °C for 20 min.

2.4.2 Gas Chromatography/Flame Photometric Detector (GC/FPD) Analysis of HD.

A Hewlett Packard Model 5890 GC was used with a flame photometric detector (FPD) and a sulfur filter. Quantitation was via HP3365 Chemstation software. A HP5 capillary column (10 m x 0.530 mm (i.d.) x 2.65 μm film thickness) was used with helium carrier gas at 2.20 mL/min constant flow mode. One μL was injected via the autoinjector in split injection mode (split ratio 45.5/1). Both the injection port temperature and detector temperature were 200 °C. Initial oven temperature was 135 °C for 1 min followed by a programmed rate of 3 °C/min to 180 °C which was held for 2 min. Chloroform was used as the solvent, and HD eluted at approximately 4.4 min. The response was calibrated with a series of HD samples of concentrations over the range 100-1000 ng/μL.

2.4.3 Nuclear Magnetic Resonance (NMR) Experiments.

Samples were analyzed using a Varian VXR-400S Fourier Transform (FT) NMR spectrometer which operates at 400 MHz for ^{1}H spectra and at 100 MHz for ^{13}C spectra. All spectra were obtained at probe temperature (22 $\pm$ 1 °C) with double precision data accumulation. Samples were provided in $CDCl_3$, D_2O, or water. All samples run in $CDCl_3$ were referenced to internal tetramethylsilane (TMS) using the $CHCl_3$ resonance ($\delta^{1}H$, 7.26; $\delta^{13}C$, 77.0) as a secondary reference. ^{1}H spectra in D_2O and water were referenced to the residual HDO/H_2O resonance (δ4.80). ^{13}C spectra in D_2O/water were referenced to external sodium 3-trimethylsilylpropionate-2,2,3,4-d_4 (TSP) in D_2O. Quantitative data were obtained by digital integration of peak areas.

^{1}H spectra were run for product identification using a sweep width of 8000 Hz (20 ppm), a pulse angle of at least 12 μs (30 deg), an acquisition time of 2-4 s and a pulse delay of 2-4 s. Corresponding ^{13}C spectra were acquired using a sweep width of at least 25000 Hz (250 ppm), an acquisition time of 1.6 s, and a pulse delay of 3 s. Spectra were accumulated until the desired signal-to-noise was achieved.

2.4.4 Percent Active Chlorine.

Solutions were analyzed for active chlorine by sodium thiosulfate titrations in the presence of excess potassium iodide under acid conditions. The sodium thiosulfate solution was 0.2 N and was standardized against potassium iodate.

3. RESULTS AND DISCUSSION

3.1 Stability of Aqueous HTH and NaOCl Solutions at 75 °C.

The results of bleach stability tests at 75 °C are provided in figures 2 and 3 and in tables 1 and 2. The half-life of the 4.35 wt% NaOCl was on the order of 50 hr whereas the half-life of the 10% HTH was approximately 16 hr. These results provide data for evaluation of the storage of bleach solutions; however, the stability is expected to drop dramatically in the environment of hot, oxidized HD at reduced pH.

3.2 Reactions with NaOCl and HD.

A small-scale reaction (NF-1) was run in an Erlenmeyer flask using 0.18 g HD and 25 mL bleach containing 4.3 wt% NaOCl, which provided a mole ratio of 12.5 OCl^-/HD (0.67 wt% HD and 4.27 wt% NaOCl). An exotherm of ca. 15 °C was observed. NMR and GC/MS analysis indicate that all HD was destroyed. Results of the MS analysis of a chloroform extract run by direct exposure probe/chemical ionization MS (DEP/CI) indicate the product was ca. 90% bis(2-chloroethyl) sulfone and 10% 2-chlorovinyl vinyl

Table 1. Stability of 4.35 Wt% NaOCl at 75 °C.

	TIME (min)	mL's S2O3	% NaOCl	% of initial	ln (% NaOCl)	TIME (hours)
1	0	4.670	4.345	99.999	1.469	0.000
2	10	4.620	4.298	98.929	1.458	0.167
3	50	4.610	4.289	98.714	1.456	0.833
4	980	3.840	3.573	82.226	1.273	16.333
5	1040	3.780	3.517	80.942	1.258	17.333
6	1110	3.600	3.349	77.087	1.209	18.500
7	1160	3.560	3.312	76.231	1.198	19.333
8	1235	3.650	3.396	78.158	1.223	20.583
9	1245	3.650	3.396	78.158	1.223	20.750
10	1325	3.410	3.173	73.019	1.155	22.083

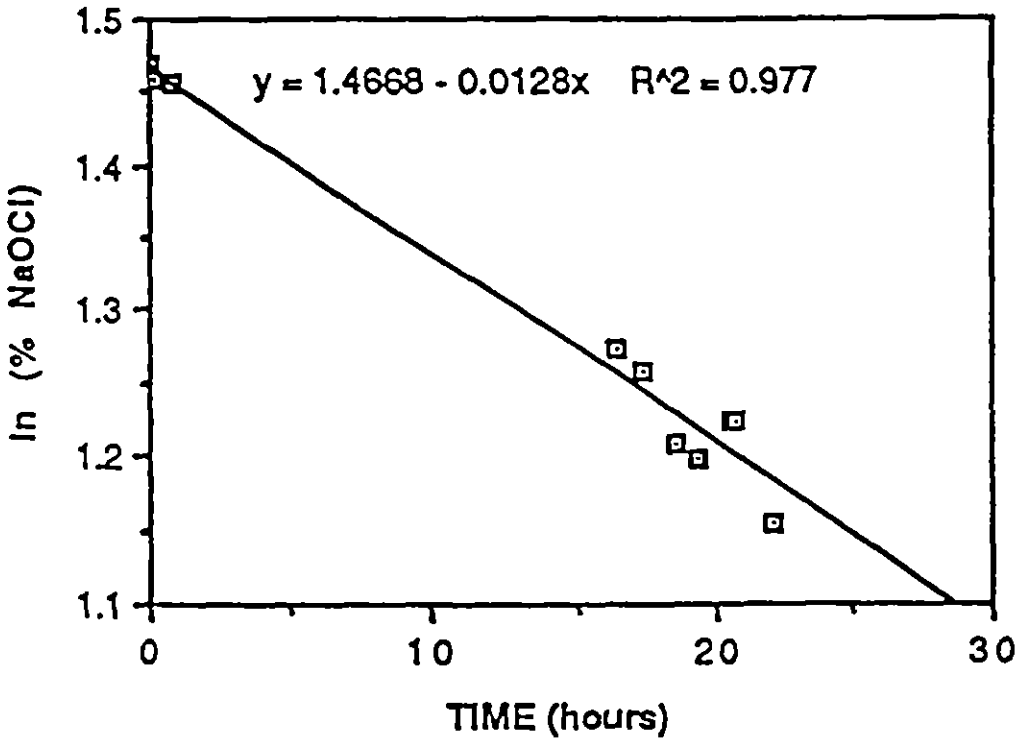


Figure 2. Stability of 4.35 Wt% NaOCl at 75 °C.

Table 2. Stability of 10% HTH (W/V) at 75 °C.

	TIME (hours)	mL's S2O3	% of initial	% Active Cl	ln % Active Cl
1	0.00	6.20	99.9	73.872	4.302
2	0.00	6.21	100.1	73.992	4.304
3	6.90	4.42	71.2	52.664	3.964
4	6.90	4.38	70.6	52.187	3.955
5	22.66	2.17	35.0	25.855	3.253
6	22.66	2.17	35.0	25.855	3.253
7	29.05	1.73	27.9	20.613	3.026
8	29.05	1.70	27.4	20.255	3.008

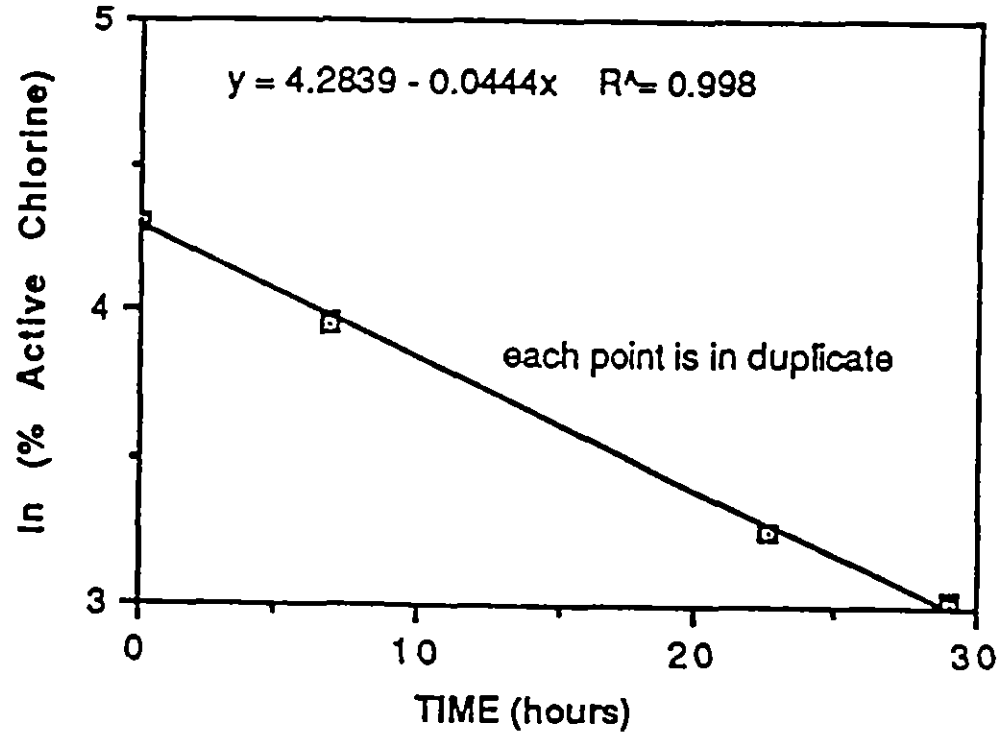


Figure 3. Stability of 10% HTH (W/V) at 75 °C.

Table 3. GC/MS/CI of NaOCl/HD Reaction Product NF-1 ($CHCl_3$ Extract).

Compound	Area Percent	
	Chloroform Layer[1]	Water Layer[2]
$CH_2=CH-SO_2-CH=CH_2$	0.5 - 10	4
$ClCH=CH-SO_2-CH=CH_2$ or Isomer	0.2 - 3	2
$ClCH_2CH_2-SO-CH_2CH_2Cl$	0.1 - 1	-
$CH_2=CH-SO_2-CH_2CH_2Cl$	32 - 64	32
$ClCH=CH-SO_2-CH_2CH_2Cl$ or Isomer	3 - 5	6
$ClCH_2CH_2-SO_2-CH_2CH_2Cl$	15 - 62	55

[1]The extract was analyzed 5 times (twice directly and 3 times after derivatization with BSTFA). The same compounds were observed in the derivatized samples as in the $CDCl_3$ extract. No thiodiglycol-related compounds were observed in the derivatized sample. The range of values obtained in the 5 runs is presented.

[2]The water sample was blown down and derivatized with BSTFA. No derivatized products were identified.

sulfone. The water layer by DEP/CI indicated the same compounds, with ca. 75% bis(2-chlorovinyl) sulfone and 2% 2-chlorovinyl vinyl sulfone observed. The results of the derivatization of the two layers and the analysis by GC/MS/CI are provided in table 3. No thiodiglycol (TDG) related compounds were observed in the derivatized product indicating sufficient OCl^- was used to oxidize all of the HD.

The preceding reaction was repeated using the small-scale vacuum jacketed glass reactor fitted with both a pH probe and a thermocouple. The recorder trace of pH and temperature vs time are presented in figure 4. The pH probe appeared to interfere somewhat with the mixing as indicated by a distorted vortex. No analyses were run on this reaction.

It was observed during the reactions in the glass reactor that as the exotherm occurred, the small droplets of HD coalesced, became cloudy, and finally disappeared into a single liquid phase. This observation suggests that the decomposition products aid in the phase transfer process and thus cause the reaction rate to accelerate.

Table 4 provides reaction data for four additional reactions with NaOCl and HD. At a mole ratio of 6.25/1 OCl^-/HD, all active chlorine was depleted.

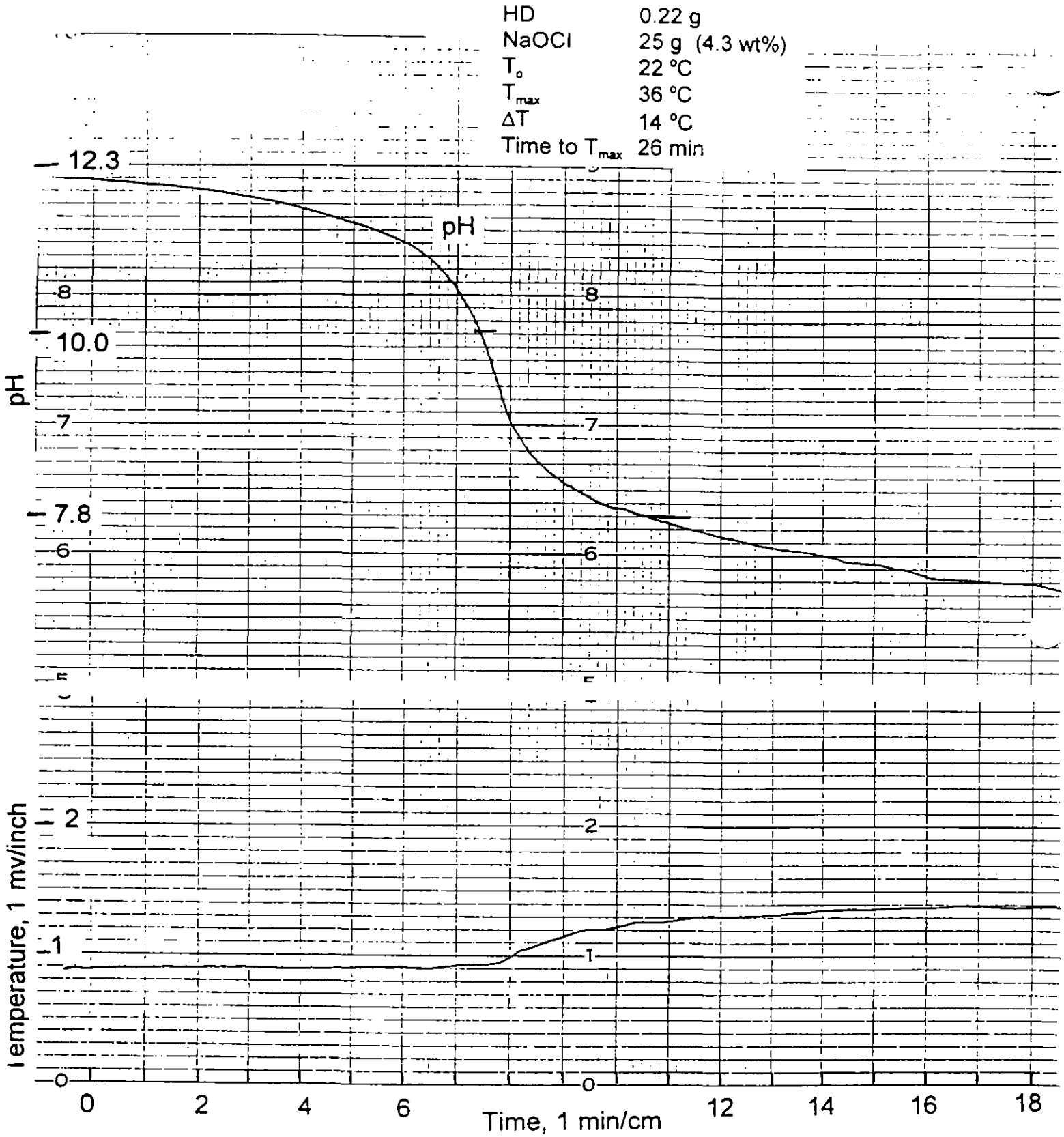


Figure 4. Reaction NG-1: pH and Temperature vs Time.

Table 4. NaOCl/HD Reaction Data.

Mole Ratio OCl/HD	Time (hours)	Initial Conc[1] (M)	Final Conc[2]	pH	% Active Chlorine[3]
12.5	1	0.046	None	6.0	0.65
12.5	24	0.046	None	3.3	0.15
6.25	1	0.092	Unknown[4]	2.2	0
6.25	24	0.092	Unknown[4]	NA	0

[1]If HD went into solution. [2]Based on chloroform extraction and GC analysis. [3]Initial 4.3 wt % Bleach with 2.0 wt % Active Chlorine. [4]Large 2-chloroethyl monovinyl sulfone peak interferes with analysis. A small HD peak could be hidden. Method was later modified.

Table 5. Reaction Data, HD and Thiodiglycol with Aqueous HTH.

Reaction No.	GR-1	GR-2	GR-3	GR-4	GR-5	GR-6
HD (in g)	0.45	0.45	0.45	0.90	1.57	-
TDG (in g)	-	-	-	-	-	0.61
HTH (in g)	3.01	3.00	3.03	3.04	3.0	3.0
Water (in g)	30.0	30.0	30.0	30.1	30.0	30.0
Mole Ratio, OCl^-/HD	10/1	10/1	10/1	5/1	2.9/1	-
T_o (°C)	26	52	60.5	25	27	28
T_{max} (°C)	47	76.5	94	59 (61)[1]	51 (52)[1]	38
delta T (°C)	21	24.5	33.5	36	25	10
Time to T_{max} (min)	13	2	0.5	3.5 (7.5)[1]	3.5 (8)[1]	<0.5
% Active Chlorine @1hr	0.30	0.09	None	None	None	1.4
pH @1 hr	4-5	1.6	1.9	1.6	1	11.7
%HD Destroyed	NA	NA	100	99.4	95	-

[1]The first value is at the end of the main exotherm. The second value is at the final maximum temperature.

Table 6. Reaction Data, HD/Aqueous HTH.

Reaction No.	GR-7	GR-8	GR-9	GR-10	GR-11	LS-1
HD (in g)	0.90	1.57	1.57	3.09	1.16[1]	60[1]
HTH (in g)	3.0	3.0	3.0	3.0	3.0	200
Water (in g)	30.0	30.0	30.0	30.0	30.0	2000
NaOH (in g)	0.5	1.0	-	1.0	1.0	66.7
Mole Ratio, OCl^-/HD	5/1	2.9/1	2.9/1	1.45/1	3.88/1	5/1
T_o (°C)	29	28	26	27	27	32
T_{max} (°C)	79	79	71.5	78	75	79 (92)[2]
delta T (°C)	50	51	45.5	51	48	60
Time to T_{max} (min)	7.5	8	3.5	6.2	13	9 (14)[2]
% Active Chlorine @1 hr	None	None	None	None	None	None
pH at 1 hr	6.1	6.4	0.6	6.2	10.0	10.5
% HD Destroyed	100[3]	99.5[3]	94	94[3]	99[3]	100[3,4]

[1]Ton container HD. [2]The first value is at the end of the main exotherm. The second value is at the maximum temperature. [3]Some hydrolysis occurred. [4]After 240 min. At 50 min, 87% of agent was destroyed.

3.3 Reactions with HTH and HD.

3.3.1 Unstabilized Reaction Studies.

Ten reactions were run with HTH and HD in the small-scale vacuum jacketed glass reactor. The reaction parameters are presented in tables 5 and 6; a TDG/HTH reaction is included in table 5 for comparison.

A series of three reactions were run with HTH and HD at a mole ratio of 10/1 OCl^-/HD (1.34 wt% HD and 9.0 wt% of 67% active HTH) to determine the effect of starting temperature on the reaction. As the starting temperature was increased from 26 to 60.5 °C, the exotherm became sharper with the delta T increasing from 21 to 33.5 °C and the time to delta T decreasing from 13 to 0.5 min. Analysis of a $CHCl_3$ extract of the GR-3

Table 7. GC/MS/CI of Reaction Product GR-5.

SCAN (sec)	COMPOUND	AREA %
269	$CH_2=CH-SO_2-CH=CH_2$	1.5
309	$ClCH=CH-SO_2-CH=CH_2$ or Isomer	0.1
352	HD	8.9
416	$ClCH=CH-SO_2-CH=CHCl$ or Isomer	0.5
448	$ClCH=CH-SO_2-CH=CHCl$	0.3
472	$CH_2=CH-SO_2-CH_2CH_2Cl$	52.9
478	$ClCH=CH-SO_2-CH_2CH_2Cl$ Isomers	2.4
512		0.3
542	$ClCH=CH-SO-CHCl-CH_2Cl$ or Isomer	0.2
581	$ClCH=CH-SO_2-CHCl-CH_2Cl$ or Isomer	0.6
586	$ClCH=CCl-SO-CCl=CHCl$ or Isomer	1.7
664	$ClCH_2CH_2-SO_2-CH_2CH_2Cl$	24.4
673	$ClCH=CCl-SO-CHCl-CH_2Cl$	3.4
687		1.3
713	$ClCH_2CHCl-SO-CH_2CH_2Cl$ or Isomer	1.1
756	$ClCH=CCl-SO-CHCl-CH_2Cl$ or Isomer	0.3

product by NMR and GC/MS indicated that no HD was present. The exotherm of reaction GR-2 is presented in figure 5.

The mole ratio was dropped to 5/1 OCl^-/HD (2.64 wt% HD and 8.93 wt% of 67% active HTH) for reaction GR-4 which was started at ambient temperature. With twice the HD as reaction GR-1, the delta T was 70% greater and the time to the main exotherm was reduced to 3.5 min. GC/MS analysis indicated that ca. 0.6% of the HD survived the reaction. The quantity of HD was doubled again for reaction GR-5, to a mole ratio of 2.5/1 OCl^-/HD (4.54 wt% HD and 8.63 wt% of 67% active HTH); however, the exotherm was reduced significantly. The temperature profile of the final stage of the exotherm indicates an extremely rapid temperature rise which ends abruptly. GC/MS results for reaction product GR-5 (table 7) show the large variety of chlorinated compounds formed during the reaction.

The rapid temperature rise is believed to be due to the increased reactivity of the active chlorine which is suddenly

HTH	3 g
HD	0.45 g
Water	30.0 g
T_o	52 °C
T_{max}	76.5 °C
delta T	24.5 °C
Time to T_{max}	2 min

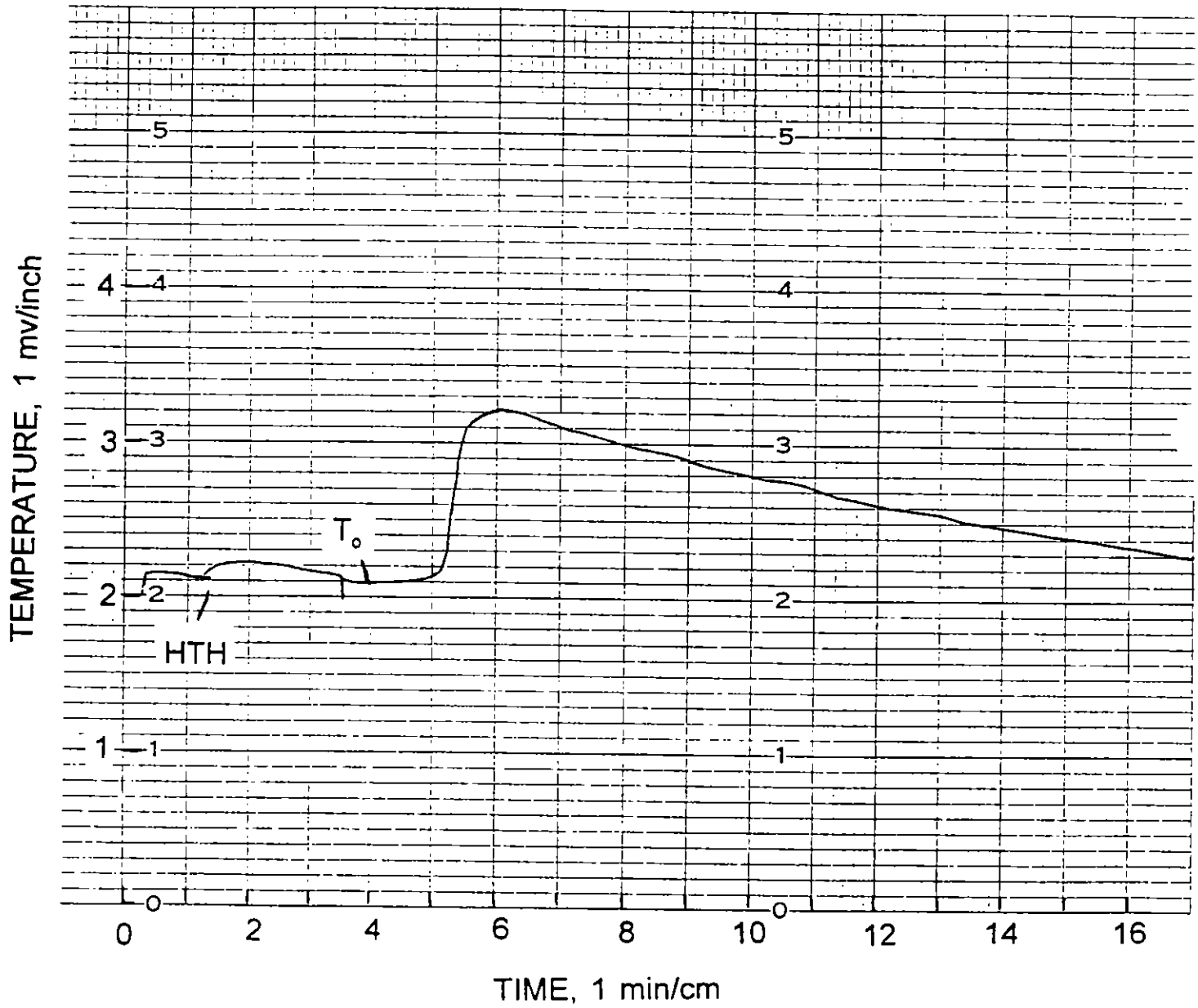


Figure 5. Reaction GR-2: HD/Aqueous HTH (Temperature vs Time).

Table 8. Reaction Data for Stabilized and Unstabilized HTH/HD Reactions.

Reaction Number	GR-4	GR-5	GR-7	GR-8	GR-9	GR-10
Mole Ratio (HTH/HD/NaOH)	5/1/0	2.9/1/0	5/1/2.2	2.9/1/2.5	2.9/1/0	1.5/1/1.3
T_o (°C)	25	26	29	28	26	27
T_{max} (°C)	59 (61)[1]	51 (52)[1]	79	79	71.5	78
Delta T (°C)	36	25	50	51	45.5	51
Time to T_{max} (min)	3.5 (7.5)[1]	3.5 (8)[1]	8	8	3	7
pH (at 1 hr)	1.6	1	6.1	6.4	0.6	6.2 (2 hr)

[1]The first value is at the end of the main exotherm. The second value is at the final maximum temperature.

released as the pH plummets. Much of the released active chlorine reacts; however, due to the nonhomogeneous nature of the system (i.e., imperfect mixing and reduced solubility of chlorine at elevated temperatures), some loss occurs.

The sharpness of the exotherm aids in evaluating the magnitude of the heat generated, since a rapid temperature rise occurs before a large portion of the heat is dissipated to the surroundings. For reaction GR-3, a heat of reaction of -375 kcal/mole HD was calculated from the exotherm observed without accounting for heat loss to the reactor or surroundings. The heat of reaction for the oxidation of HD following the worst case (eq. 1) was estimated to be ca. -1040 kcal/mole of HD.*

3.3.2 Stabilized HTH Reaction Studies.

Several additional tests were run to determine if the reaction could be controlled and additional HD destroyed by stabilizing the HTH. Various methods have been reported for stabilization of HTH for field use[4] including utilizing caustic to prevent an excess drop in pH. Because of its relatively high solubility in water, NaOH was used in these studies. Three reactions (GR-7, GR-8 and GR-10) were run with stabilized HTH; one additional unstabilized reaction (GR-9) was also run. The results of these reactions are presented in tables 6 and 8.

* Estimated value at 25 °C based on literature values for heats of formation. (Personal communication, Elwin C. Penski, Research and Technology Directorate, ERDEC, 9 Jun 93).

Table 9. Analysis of Reaction Product GR-8 by GC/MS and NMR.

COMPOUND	GC/MS[1] Aqueous Layer Area %	NMR[2] $CHCl_3$ extract Mole %
CH_2=CH-SO-CH=CH_2	32.7	88
HD	-	5
$HOCH_2CH_2SCH_2CH_2OCH_2CH_3$, TMS DER	7.2	-
$HOCH_2CH_2SCH_2CH_2OH$, DI-TMS DER	60.1	-
$HOCH_2CH_2SCH_2CH_2OH$	-	4
Other	-	2

[1]CI analysis product derivatized using BSTFA. [2]Combined ^{13}C and ^{1}H NMR.

In reaction GR-7 (2.62 wt% HD, 8.72 wt% of 67% active HTH, and 1.45 wt% NaOH), 0.5 g NaOH was used to stabilize the system. Based on the temperature profile compared to the unstabilized reaction GR-4, the reaction proceeded initially in a sedate and controlled manner until ca. 75% through the exotherm at which point the rate of heat production accelerated suddenly. The final pH at 1 hr was 6.1 compared to 1.6 for a similar unstabilized reaction. It was felt that the NaOH stabilizer was depleted at the latter stages of the exotherm allowing the pH to drop to a level that destabilized the bleach.

In reaction GR-8, the quantity of NaOH stabilizer was increased to 1.0 g to provide stabilization throughout the reaction. HTH (3 g) and 1.57 g HD (4.41 wt% HD, 8.43 wt% of 67% active HTH, and 2.81 wt% NaOH) were used to match the mole ratio of 2.9/1 OCl^-/HD in GR-5. GC/MS and NMR results of reaction GR-8 are presented in table 9. Reaction GR-9 (4.54 wt% HD and 8.67 wt% of 67% active HTH) was identical to GR-8 except no stabilizer was used. The exotherms of reactions GR-8 and GR-9 are presented in figure 6 and illustrate the effect of NaOH as a stabilizer: The resulting exotherm was more gradual, a higher delta T was observed, and more HD was destroyed.

Reaction GR-10 (8.33 wt% HD, 8.09 wt% of 67 % active HTH, and 2.70 wt% NaOH) was run to determine what would happen under extremely rich HD conditions (table 8).

The difference in the exotherms of GR-5 and GR-9 underscore the value of a stabilizer. Small differences in mixing or drop size in the two phase reaction at the time that

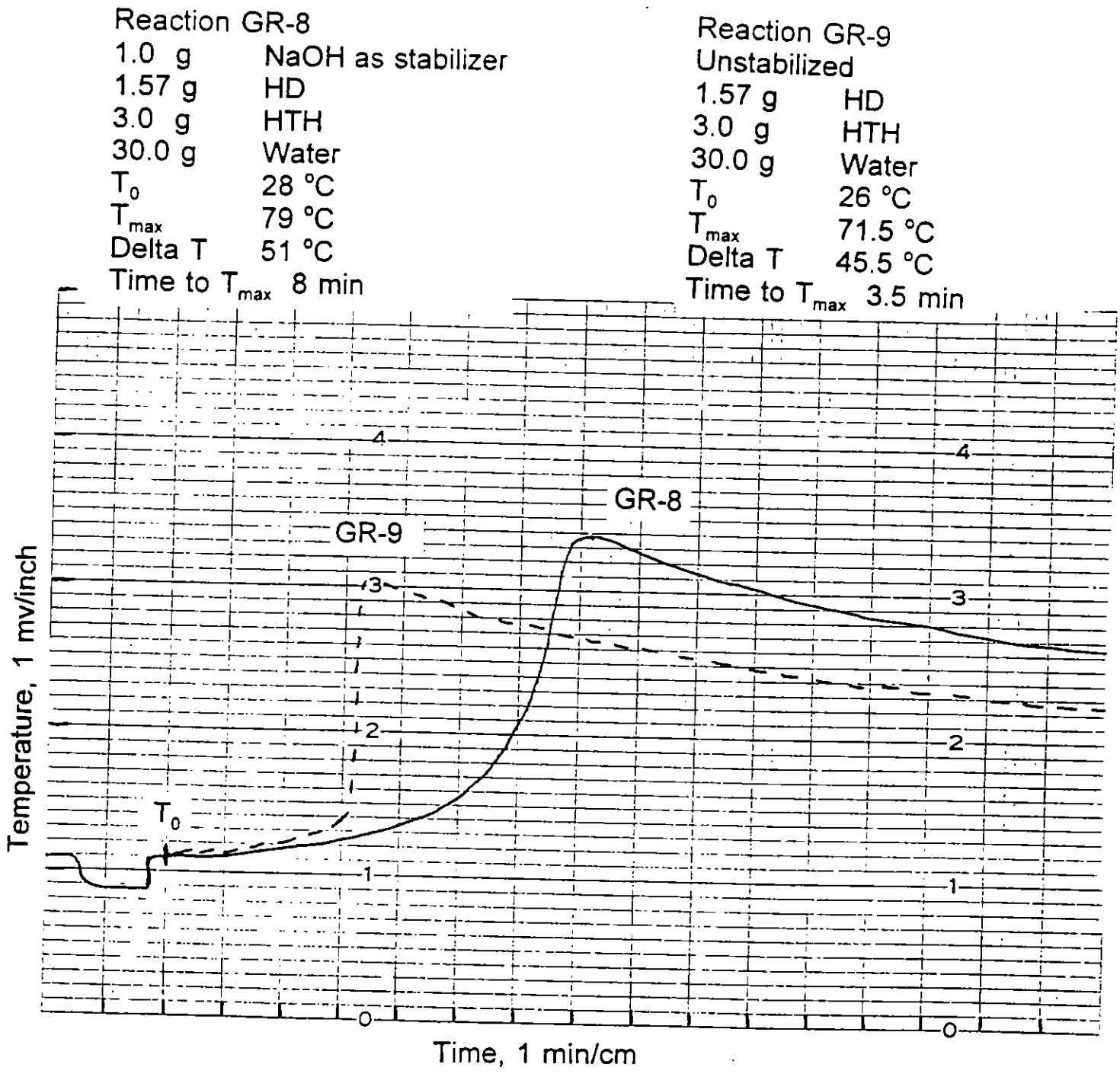


Figure 6. Exotherms of Stabilized and Unstabilized HD/HTH Reactions.

the OCl^- is suddenly released have a large effect on the ability of the HD to react with the escaping active chlorine.

Exotherms resulting from reactions using base stabilized HTH appear to be independent of the amount of HD used over the range studied (5/1 to 1.5/1, molar ratio OCl^-/HD). In each case, starting at ca. 25 °C, the temperature rise was ca. 51 °C and occurred over ca. 8 min.

3.3.3 Ton Container HD Studies.

Small Scale-Reaction Study.

One reaction (GR-11) was run in the small-scale glass reactor using 3.88/1 mole ratio OCl^-/ton container HD with the HTH stabilized with NaOH (3.30 wt% HD, 8.53 wt% of 67% active HTH, and 2.54 wt% NaOH). The exotherm (figure 7) was slightly delayed in starting and occurred at a slower rate than observed for pure HD at various mole ratios. The most dramatic difference between the ton container reaction and the other stabilized reactions (GR-7, GR-8 and GR-10, table 6) was that the pH only dropped to 10 despite the consumption of all active chlorine. The relatively sedate reaction suggests that more of the active chlorine reacted with the sulfides in the ton container HD than in the pure HD, which resulted in the formation of fewer acids.

Mid-Scale Reaction.

Ton container HD (60 g) was reacted (LS-1) with a solution made of 200 g HTH, 66.7 g NaOH and 2000 mL distilled water (2.58 wt% HD, 8.60 wt% of 67% active HTH, and 2.87 wt% NaOH) giving a mole ratio of 5/1, OCl^-/HD (figure 8 and table 6).

The initial exotherm peaked at 9 min and resulted in a temperature rise from 32 to 79 °C. The temperature continued to rise gradually to 92 °C for an additional 5 min. GC analysis of a sample drawn and extracted into chloroform at 50 min indicated that 87% of the initial HD was destroyed. Analysis of samples drawn at 2.4 and 5 hr indicated all HD was destroyed. Results of the GC/MS/CI analysis of the 50 min chloroform extract are presented in table 10. The high level of HD reported represents the chloroform layer only and not the overall sample. The GC method provides the total weight of HD detected and relates back to the total sample. The pH at 1 hr was 10.5, consistent with the small-scale stabilized ton container reaction. The continued gradual temperature rise after the initial exotherm is believed to result from hydrolysis of the HD and other compounds, since essentially all of the OCl^- is consumed during the first exotherm.

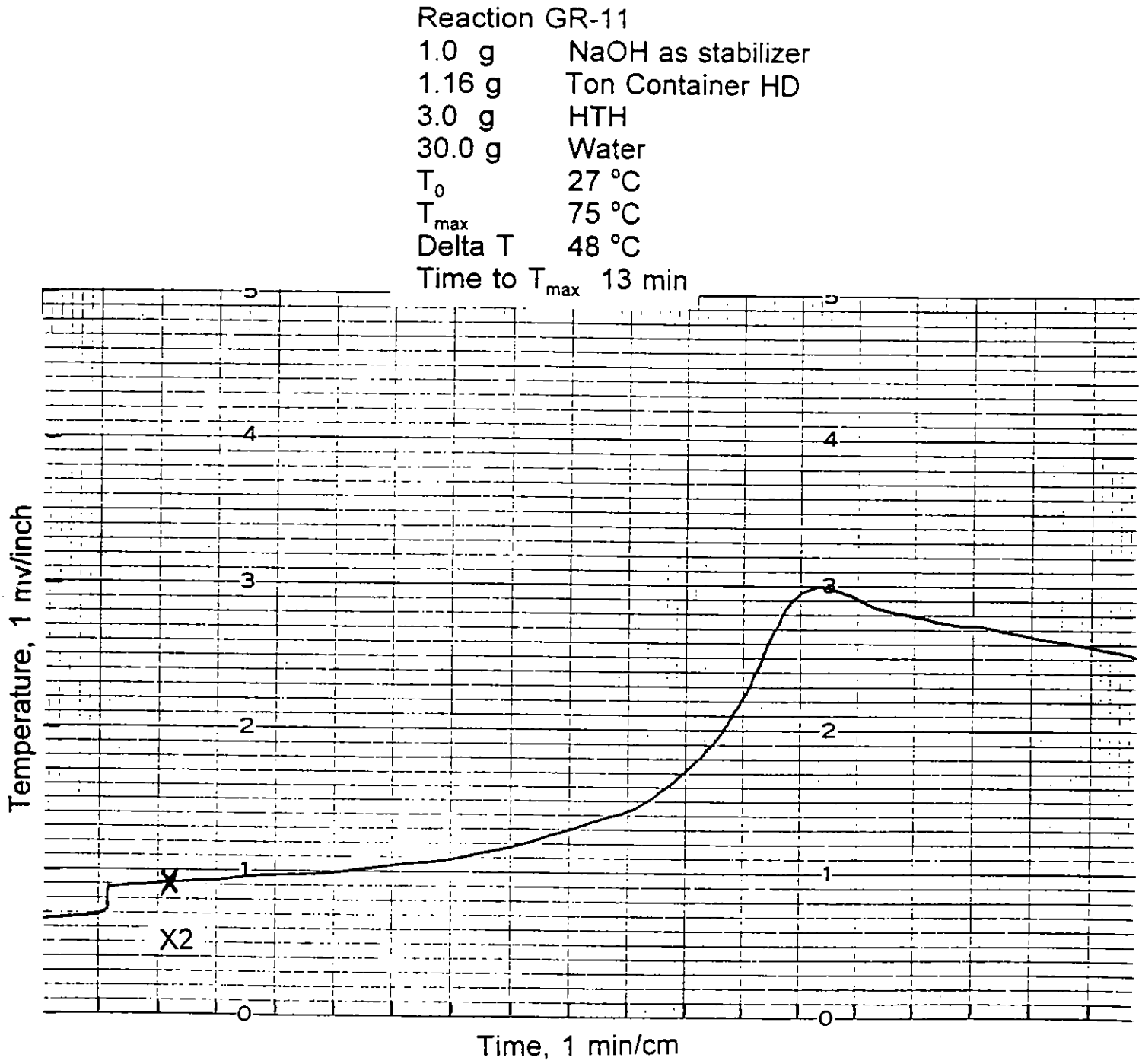


Figure 7. Exotherm of Reaction of Ton Container HD with Stabilized HTH.

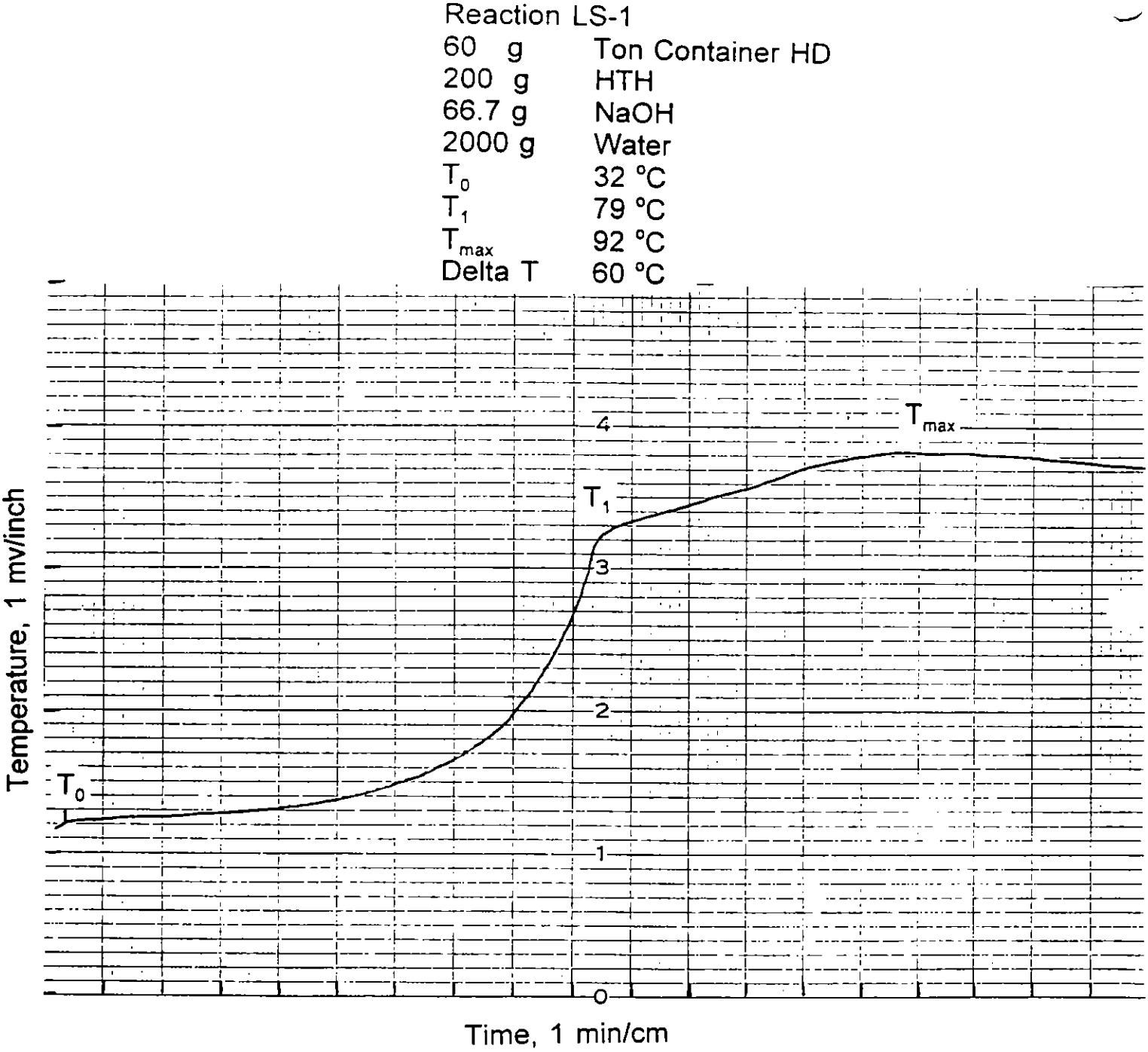


Figure 8. Exotherm of Mid-Scale Reaction of Ton Container HD with Stabilized HTH.

Table 10. GC/MS Analysis of Mid-Scale Reaction Product at 50 Min ($CHCl_3$ Extract).

COMPOUND	AREA %
CH_2=CH-SO-CH=CH_2 or CH_2=CHSCH_2CHO	14.7
HD	63.5
$ClCH_2CH_2SCH_2CH_2CH_2Cl$	0.5
$ClCH_2CH_2SC_4H_8Cl$ Isomers	0.8
	0.7
	3.4
Unknown (molecular weight = 136)	1.0
$ClCH_2CH_2SSCH_2CH_2Cl$	0.6
$ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$	14.9

3.4 The Reaction of HTH with Thiodiglycol (TDG).

One reaction with TDG and HTH was run to study the oxidation of the sulfur to sulfone in a single phase system. Using the small-scale glass reactor, 0.61 g of TDG was reacted with 3 g HTH in 30 mL water (1.8 wt% TDG and 8.9 wt% of 67% active HTH), which provided a mole ratio of 5.6/1 OCl^-/TDG. The temperature rose from 28 °C to 38 °C in less than 0.5 min. Titration of the product mixture indicated 31% of the initial active chlorine had been consumed. The final pH was 11.65. Reaction results are included in table 5.

The NMR spectrum of the product mixture showed 91 mole% of TDG sulfone and two unidentified impurities. GC/MS confirmed the sulfone and saw one major impurity which was not identified. Based on the quantity of active chlorine consumed, ca. 1.8 moles of OCl^- was required to convert each mole of TDG to the sulfone. Thus, without interfering compounds, TDG was found to be oxidized according to the following reaction:

$$(HOCH_2CH_2)_2S + Ca(OCl)_2 \longrightarrow (HOCH_2CH_2)_2SO_2 + Ca(Cl)_2 \qquad \text{(Eq. 2)}$$

The TDG reaction with OCl^- was different from the HD reactions in that the TDG was a single phase reaction and the reaction stopped at the sulfone despite the presence of excess OCl^-. Based on the exotherm, the TDG reaction was essentially

complete in less than 30 sec. The observed heat of reaction for the oxidation of the TDG to the sulfone was ca. -64 kcal/mole compared to -375 kcal/mole observed for the HD reaction (GR-3) with assorted side reactions. In both cases, the observed heat does not include heat lost to the glass reactor.

4. CONCLUSIONS

Two moles of OCl^- are required to oxidize one mole of HD to the sulfone; however, several additional moles of OCl^- are consumed in competing side reactions. Many factors including mixing, purity, temperature, and degree of bleach stabilization affect the amount of OCl^- required. Based on the reactions with stabilized aqueous OCl^-, the lowest mole ratio that might be expected to oxidize all of the HD to the sulfone was in the range of 5-6 moles OCl^- to 1 mole HD.

The drop in pH encountered during the reaction of HD with bleach dramatically reduces the stability of the OCl^-. Rapid release of chlorine occurs which results in excessive side reactions and the escape of some chlorine.

The OCl^-/HD reaction can be moderated using NaOH to maintain an elevated pH throughout the reaction which stabilizes the OCl^-. The slower, more controlled reaction provides more time for mixing of the two phase system which allows the chlorine to come in contact with and destroy more HD. The moderated reaction results in fewer side products and the oxidation of additional HD.

Small droplets of HD appear to grow and become cloudy during the exotherm suggesting that the decomposition products become a better phase transfer medium for the HD and OCl^- which results in an acceleration of the reaction.

While true kinetic data have not been obtained, essentially all oxidation (except in the reactions with a high ratio of OCl^-) is complete once the exotherm is over due to depletion of OCl^-. It is assumed that the temperature profile indicates roughly the progress of the reaction. Because there are two liquid phases, the reaction is initially very slow. However, the rate accelerates as decomposition products are formed and enhanced phase transfer occurs.

Significant heat (greater than 375 kcal/mole of HD) is produced during the destruction of HD with bleach.

The oxidation of ton container HD requires a greater quantity of active chlorine than pure HD probably because of the oxidation of additional sulfide impurities present in the ton container agent.

Once the OCl^- is depleted, hydrolysis will continue to slowly destroy the remaining HD if sufficient NaOH is used to stabilize the system and maintain an elevated pH throughout the HTH/HD reaction.

After depletion of the active chlorine, the overall hydrolysis process for HD and other products in the system is exothermic based on the temperature profile of the mid-scale reaction run with ton container HD.

5. RECOMMENDATIONS

Neither NaOCl nor $Ca(OCl)_2$ is recommended for stockpile decontamination of HD for the following reasons:

- The overall OCl^-/HD reaction, including side reactions, is very exothermic amounting to more than -375 kcal/mole of HD.

- Two moles OCl^- are required to oxidize one mole of HD to the sulfone; however, competing side reactions consume several additional moles of OCl^-.

- A variety of both highly chlorinated and unsaturated compounds are formed during the HD oxidation. The multiplicity of products complicates assessments of toxicity.

Both $Ca(OCl)_2$ and NaOCl are, however, still effective decontamination materials for HD where the above stated concerns are of lesser importance.

When less then a 14/1 mole ratio of OCl^-/HD is used, caustic should be used as a stabilizer to prevent an excessive drop in pH and the subsequent rapid release of chlorine. If a high pH is maintained throughout the reaction, any unoxidized HD will be gradually hydrolyzed after the OCl^- is depleted.

If $Ca(OCl)_2$ or NaOCl are used for large scale destruction of HD, sufficient caustic stabilizer should be used to maintain an elevated pH in order to moderate the reaction. Stabilization of the system should result in a lower requirement for bleach, fewer side products, and less heat generated per mole of HD reacted.

LITERATURE CITED

1. Yurow, H.W., and Davis, G.T., Decontamination and Disposal Methods for Chemical Agents - A Literature Survey, ARCSL-TR-81080, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, November 1982, UNCLASSIFIED Report (AD-B069 586).

2. Durst, H.D. et. al., Support for the Delisting of Decontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD02 in COMAR 10.51.02.16-1, CRDEC-TR-009, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November 1988, UNCLASSIFIED Report (AD-A271 648).

3. Yang, Y.-C., Baker, J.A., and Ward, J.R., "Decontamination of Chemical Warfare Agents," Chem. Rev. Vol. 92, No. 8, p. 1729, 1992.

4. Mankowich, I., et. al., History of Research and Development of the Chemical Warfare Service Through 1945, Decontamination of Chemical Agents, Part II, EASP 300-5, Edgewood Arsenal, MD, September 1970, UNCLASSIFIED Report (AD-872 030).

IDENTIFICATION OF THE ISOMERIC FORMS OF LEWISITE USING MASS SPECTROMETRY, NUCLEAR MAGNETIC RESONANCE AND INFRARED SPECTROSCOPY, AND MOLECULAR MODELING

John R. Smith, Thomas P. Logan, Robert L. Von Tersch, Edward M. Jakubowski, Theodore W. Dolzine, Linda L. Szafraniec*, and Joseph J. Urban*

U.S. Army Medical Research Institute of Chemical Defense and
*U.S. Army Edgewood Research, Development & Engineering Center
Aberdeen Proving Ground, MD 21010

ABSTRACT

Our research has identified a previously unreported form of lewisite, a geminal isomer. We have attempted to characterize this isomer along with the previously reported geometric isomers of lewisite using several spectroscopic methods and a molecular modeling program. Proton NMR produced a coupling constant consistent with vinylic protons in a geminal configuration. Attempts at examining the geminal isomer using proton coupled ^{13}C NMR were unsuccessful due to the small percentage of the geminal isomer in the neat material. The direct injection of lewisite onto a gas chromatograph resulted in a variety of deleterious effects that were observed after only a few injections. Therefore the gas chromatographic separation and subsequent detection by mass spectrometry and infrared spectroscopy was based on an ethanedithiol derivative of the lewisite. The mass spectra of the trans and cis derivatives were very similar, but the gem form displayed significant differences. The sensitivity of the infrared method employed only produced spectra for the trans and gem derivatives with significant differences observed between the two. Molecular modeling calculations indicate that the trans and cis stereoisomers have similar dipole moments while the geminal isomer has a slightly higher dipole moment.

INTRODUCTION

Lewisite (dichloro(2-chlorovinyl)arsine) (L) is a potent blister agent that was originally developed for use as a chemical warfare agent during the later stages of World War I. As a result of its late introduction, it was not utilized in combat. Interest in lewisite and other arsenicals resurfaced at the beginning of World War II. Due to a variety of factors which include the discovery of an effective antidote, lewisite quickly fell out of favor as a suitable warfare agent. Despite this, there are reportedly significant stockpiles of lewisite currently being held

by both Russia and the United States. In January of 1993 at the Chemical Weapons Convention in Paris, 130 nations signed an historic multi-lateral arms control agreement. One of the provisions of this chemical weapons treaty calls for the destruction of the major portion of weapons stockpiles. Verification requirements have created a renewed interest in analytical methodologies for all chemical warfare agents including lewisite and related compounds.

Lewisite is prepared from the reaction of acetylene and arsenic trichloride in the presence of a catalyst. Aluminum chloride, mercuric chloride, and cuprous chloride are the predominate catalysts employed with approximate yields of 20, 80-85, and greater than 85% reported, respectively. Other reaction products reported are bis(2-chlorovinyl)chloroarsine (L-2) and tris(2-chlorovinyl)arsine (L-3).[1]

During the course of developing analytical methods for lewisite, what is believed to be a positional isomer of lewisite, a geminal form, was discovered. The geminal isomer, dichloro(1-chlorovinyl)arsine, was in fact found to be in greater abundance than the cis isomer. In reviewing the literature, we could not find any reference which lists the geminal isomer as a reaction product from lewisite synthesis. The lewisite product has been reported as a mixture of two isomers with one form always of greater abundance. The more abundant isomer was designated during the 1940's as trans-lewisite based on dipole moment[2] and electron diffraction.[3] More recently this designation was confirmed by Paasivirta et al. using NMR.[4] The less abundant isomer (referred to as "*iso*lewisite" or lewisite Isomer II) was assigned the cis configuration based on dipole moment alone.[2] Electron diffraction data did not exclude the possibility of a geminal isomer.[3] A more recent publication from the Ministry of Foreign Affairs of Finland provided NMR confirmation of cis-lewisite and also reported gas chromatographic retention data.[5] Ali-Mattila et al. reported mass spectra for the cis isomer.[6] Other reports have designated a lewisite isomer as the cis form, but their data was not consistent with the previously reported retention data or mass spectra.[7,8]

This work attempts to characterize the geminal isomer of lewisite using mass spectrometry (MS), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and a molecular modeling program. The coupling constants observed for ^{1}H NMR were consistent with a geminal alkene. A gas chromatographic (GC) method was developed that provides a means of analytically separating the three isomers. Due to the corrosive nature of lewisite on the analytical instrumentation, the method was based on a dithiol derivative of the lewisite.[9] In our investigation, mass spectrometry (MS) coupled with gas chromatography was the only analytical method sensitive enough to observe all three isomers in our solutions of lewisite. The electron ionization (EI) mass spectrum of the geminal derivative differed considerably from that observed for the two stereoisomers. We were only able to record an infrared (IR) spectrum for the trans and gem derivatives of lewisite. The major

features of the trans spectrum are similar to those reported for underivatized lewisite[3,18] as well as for L2 and L3.[18] The gem derivative also contained some of the same absorption bands but had several distinguishing features. Dipole moments of the three isomers were calculated using a molecular modeling program. Our calculations indicate that the trans and cis isomers have dipole moments very close to one another while the geminal dipole moment is greater.

EXPERIMENTAL

Nuclear Magnetic Resonance Spectroscopy (NMR)

Both ^{1}H and ^{13}C NMR spectra were recorded using a Varian VXR-400S super-conducting FTNMR spectrometer system. Spectra were obtained at probe temperature (22 ± 1°C) in double precision mode. Tetramethylsilane (TMS) was used as the internal reference. The ^{1}H spectrum was obtained at 400 MHz using a sweep width of 8K Hz, a pulse width of 24° (8 µsec), an acquisition time of 4.0 seconds and a pulse delay of 4.0 seconds. The ^{13}C NMR spectrum was obtained at 100 MHz using a sweep width of 25K Hz, a pulse width of 61° (9.5 µsec), an acquisition time of 1.6 seconds, a pulse delay of 2.0 seconds, and full proton WALTZ decoupling. Approximately 20 - 30 mg of neat lewisite obtained from the U.S. Army Edgewood Research, Development & Engineering Center (Lot No. L-U-6206-CTF-N) was transferred into a 5-mm o.d. Pyrex NMR tube (Wilmad 507-PP) and 1 gram of $CDCl_3$ (MSD Isotopes) was added. The tube was shaken several times to insure homogeneity of the sample.

← distilled @ 1 Jun 92 to Linda Szatanic

Sample Derivatization

A standard stock solution of lewisite in solvent was prepared by weighing to the nearest 0.1 mg about 0.235 grams of lewisite in a tared 50-ml Class A volumetric flask and diluting to mark with hexane (HPLC grade). The lewisite used for derivatization was also obtained from USAERDEC (Lot No. L-U-4273-ICD-D). Analysis by ^{13}C NMR indicated the material was composed of trans-lewisite at 95.2 mole % and contained a major impurity of 2.7 mole %. One ml aliquots of the standard stock solution (4.54 mg/ml) were prepared and stored at -70°C for use as needed. Samples to be analyzed using gas chromatography were derivatized with 1,2-ethanedithiol (EDT) prior to injection onto the gas chromatograph. Derivatization was performed by adding 100 µl of stock lewisite solution , 900 µl of hexane, and 50 µl of 1% (v/v) EDT (Sigma, St. Louis, Mo.) in hexane. The reaction mixture was prepared in an agent approved fume hood using a 1.5 ml screw-capped vial with a teflon coated septum as a reaction vessel. All derivatizations were done at room temperature and allowed 30 minutes to go to completion. After vortex mixing, 100 µl of the reaction mixture was pipetted into a glass-lined autosampler vial. NMR analysis of the derivatized lewisite was performed on a sample produced by mixing 20 µl of neat lewisite with 60 µl of neat EDT at room temperature.

Gas Chromatography (GC)

Gas chromatographic separations were performed on a Hewlett-Packard 5890 gas chromatograph. The GC was fitted with a 30 m x 0.25 mm I.D. DB-5 bonded phase column, 0.25 μm film thickness (J&W Scientific). Helium was used as the carrier gas at a linear velocity of 35 cm s^{-1} (air injection at 60°C). The oven temperature was held initially at 60°C for 2 min, programmed from 60 to 250°C at 30°C min^{-1}, and held at 250°C for 2 min. Splitless injections of 1 μl volume were made. The split delay was set at 0.75 min., injection port temperature 250°C; split flow 40 ml min^{-1}; transfer line temperature 280°C and septum purge 2 ml min^{-1}.

Mass Spectrometry (MS)

Electron ionization GC/MS analyses were performed on a Hewlett-Packard 5971A mass selective detector interfaced to the GC above. The electron ionization MS operating conditions were as follows: ion source pressure 1.5 x 10^{-5} torr; source temperature 200°C; electron energy 70eV; electron emission current 220 μA; scan range 60 to 250 amu, and scan rate 2.44 scans sec^{-1}.

Infrared Spectroscopy (IR)

Fourier transform infrared spectroscopy analyses were performed on a Nicolet 60SX interfaced to the GC above. A liquid nitrogen cooled mercury-cadmium-telluride (MCT-A) detector was used. Chromatograms were generated using a Gram-Schmidt reconstruction. Resolution was set at 8.0-cm^{-1}. The light pipe and transfer line were both set at 200°C.

Molecular Modeling

All three isomeric forms of lewisite were examined using the Spartan electronic structure molecular modeling program (Wave Function, Inc) on a Silicon Graphics SGI-210 platform. Ab Initio calculations were performed at the STO-3G level of theory to include the calculation of dipole moment as well as a LUMO energy surface density map.

RESULTS & DISCUSSION

Vinylic protons in a trans configuration are expected to have coupling constants (J values) between 12 and 18 Hz for proton NMR whereas the coupling constants for a cis configuration are expected to range between 8 to 12 Hz. Geminal alkene protons, on the other hand, are expected to show J values between 0 and 5 Hz.[11] Thus, the J value of 14.8 Hz observed for the resonances at δ6.94 (ClC<u>H</u>=) and δ7.15 (=C<u>H</u>[$AsCl_2$]) in $CDCl_3$ was consistent for the trans isomer and in close agreement with other reported values.[4,5] The small coupling constant of 3.2 Hz observed for the resonances at δ6.22 and δ6.33 was consistent for a geminal isomer (Figure 1). The cis isomer could not be detected with the NMR. The cis isomer of lewisite has been observed by the Finnish and found to have a J value of 7.1 Hz for its two resonances at δ6.92 (ClC<u>H</u>=) and δ7.14 (=C<u>H</u>[$AsCl_2$]) in $CDCL_3$.[5] Proton coupled ^{13}C NMR reported by Paasivirta

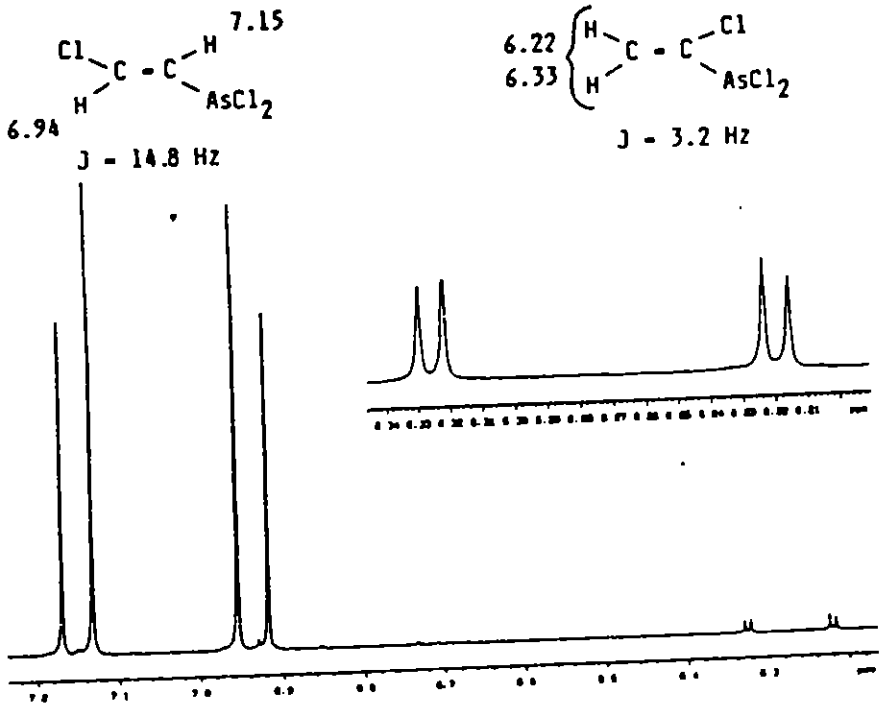
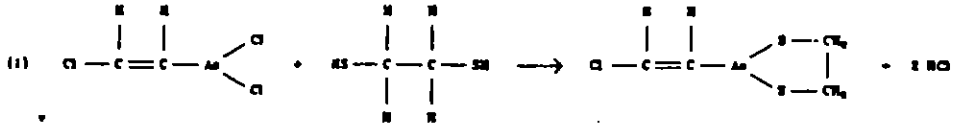


Figure 1. ^1H NMR of neat lewisite.

et al. showed that the two resonances for trans-lewisite were each a doublet of doublets (δ132.5, $^1J_{C\alpha}$ = 197.2 Hz, $^2J_{C\alpha}$ = 8.2 Hz; δ138.5, $^1J_{C\alpha}$ = 174.6 Hz, $^2J_{C\alpha}$ = 4.2 Hz).[4] This coupling pattern is consistent for protons on two adjacent carbon atoms. In our proton decoupled ^{13}C NMR experiment we observed two resonances for the trans isomer at δ133.1 and δ139.2. In addition, resonances at δ125.8 and δ146.2 were observed for the geminal isomer. The small percentage of gem lewisite in the neat material made attempts at a proton coupled experiment unsuccessful. One would expect to observe a triplet and a singlet for the resonances at δ125.8 and δ146.2, respectively. Analysis of the lewisite-EDT derivative using ^1H NMR gave results which paralleled those of underivatized lewisite. The coupling constants for the vinylic protons were 14.1 Hz (AB centered at δ6.49) for the trans derivative and 2.0 Hz (δ5.96 and δ6.02) for the gem. The amount of the geminal derivative was estimated at approximately 3% which was in close agreement with the percentage of the gem lewisite prior to derivatization.

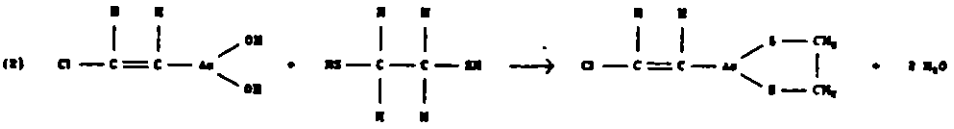
The gas chromatographic (GC) method was developed using a

dithiol derivative of lewisite.[8] EDT was selected to produce the derivative shown in reaction (1):



I

The derivative was rapidly formed at room temperature and stable for several weeks. The same derivative has also been found to form between the primary hydrolysis product of lewisite, 2-chlorovinylarsonous acid (CVAA), and EDT[8,12] according to reaction (2) :



I

Under the gas chromatographic conditions used the gem, trans, and cis isomers of the lewisite-EDT derivatives had retention times of 7.98, 8.28, and 8.33 minutes, respectively. Using a non-polar stationary phase (DB-1), the retention times shifted slightly but the elution order was maintained. The presence of arsenic in each of the isomers was confirmed using an atomic emission detector interfaced to a GC.[9] The elution order for the stereoisomers was consistent with that reported for an underivatized mixture of trans/cis (3/1 ratio, confirmed using NMR) lewisite.[8] It was not consistent for the stereoisomers reported elsewhere[7,8] and we suspect that a geminal isomer was present but mislabelled as the cis isomer. Consequently, the electron ionization (EI) mass spectra recorded in the same reports also appear to be mislabelled.

Using EI mass spectrometry, all three lewisite-EDT derivatives produced a large molecular ion at *m/z* 228 although the observed abundance for the gem derivative was less than half of that observed for the other two derivatives. The *m/z* 167 ion resulting from the dithiarsenoline ring fragment was the base peak for the gem and trans derivatives and nearly so for the cis derivative (93%). Overall, we found only minor differences in the EI mass spectra of the lewisite-EDT trans and cis derivatives (Figure 2; Table I). In general, stereoisomers can be expected to produce EI mass spectra that are very similar for both the ions observed as well as the relative abundance of each.[13,14] Ali-Mattila et al. reported that the EI mass spectra for trans and cis lewisite were identical.[8] The EI mass spectrum of the gem derivative differed substantially from the two stereoisomers. The smaller abundance of the molecular ion could possibly be explained in terms of thermochemical stability.[13] The *m/z* 165 fragment ion was nearly

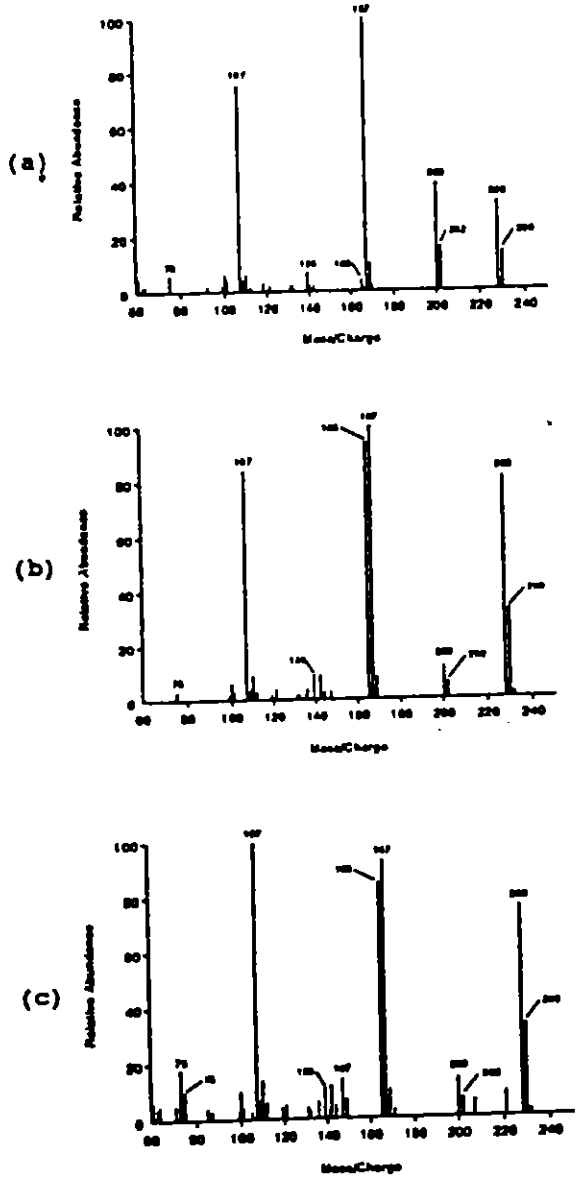


Figure 2. Electron ionization mass spectra of (a) geminal, (b) trans, and (c) cis isomers of lewisite-EDT derivative.

absent in the gem derivative (4%) while it was one of the most abundant ions for the trans and cis derivatives (94 and 85%, respectively). In addition the m/z 200 ion was much more abundant for the gem. We believe that the m/z 165 fragment ion results from loss of the chlorine ion along with loss of the C_2H_4 portion of the 5-membered ring. The possibility exists that the m/z 165 could result from loss of H_2 from the dithiarsenoline ring fragment ion (m/z 167). This was ruled out based on the lack of a m/z 165 ion for phenylarsine oxide that had been derivatized with EDT and contained the same 5-membered ring.[15] It appears that having both the chlorine and the dithiarsenoline ring attached to the same carbon (i.e., the gem derivative) results in preferrential loss of the ring structure. The trans and cis derivatives have the chlorine atom and the ring attached to different carbons and appear to lose either portion with almost the same likelihood. Characteristic "A+2" isotopic peaks produced from chlorine and sulfur were also observed.

Attempts at obtaining the infrared spectra for all three of the derivatives after gas chromatographic separation proved unsuccessful. We were only able to obtain spectra for the trans and gem derivatives (Figure 3). The most prominent absorption bands observed for the trans lewisite-EDT derivative were at 2931, 1597, 1547, 1282, 929, and 795 cm^{-1}. All but the band at 2931 cm^{-1} correspond very closely to those observed for underivitized lewisite[9,10] as well as for L-2 and L-3.[10] Absorption at 2931 cm^{-1}

Table I. Electron ionization mass spectra of lewisite-EDT derivatives (major ions).

		relative abundance (%)		
m/z	proposed structure	gem	trans	cis
230	228 "A+2" isotope [41.3]	14 (44)	33 (41)	33 (43)
228	$C_4H_6AsClS_2$	32	81	76
202	200 "A+2" isotope [41.3]	16 (41)	6 (50)	7 (50)
200	$C_2H_2AsClS_2$	39	12	14
169	167 "A+2" isotope [8.8]	10 (10)	8 (8)	10 (11)
167	$C_2H_4AsS_2$	100	100	93
165	$C_2H_2AsS_2$	4	94	85
139	AsS_2	7	9	11
107	AsS	75	84	100
75	As	6	3	10

[ ] = expected isotopic abundance
( ) = observed isotopic abundance

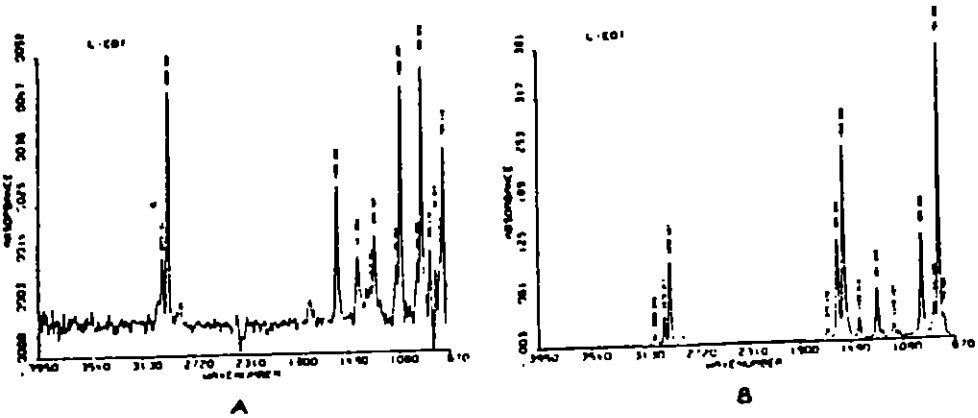


Figure 3. IR spectra of gem (a) and trans (b) L-EDT derivatives.

is characteristic for methylene groups and should result from the aliphatic portion of the EDT derivatizing agent. The gem derivative IR spectrum contained the absorption bands at 2931, 1597, 1283, and 930 cm^{-1} but lacked the 1547 and 795 cm^{-1} bands. The gem spectrum was the only one with strong absorption bands at 900 and 723 cm^{-1}. The 900 cm^{-1} band is characteristic for the CH_2 out-of-plane wag for $CH_2=CR_1(R_2)$ compounds.[16] The sensitivity of our method was not sufficient to obtain a spectrum for the cis derivative.

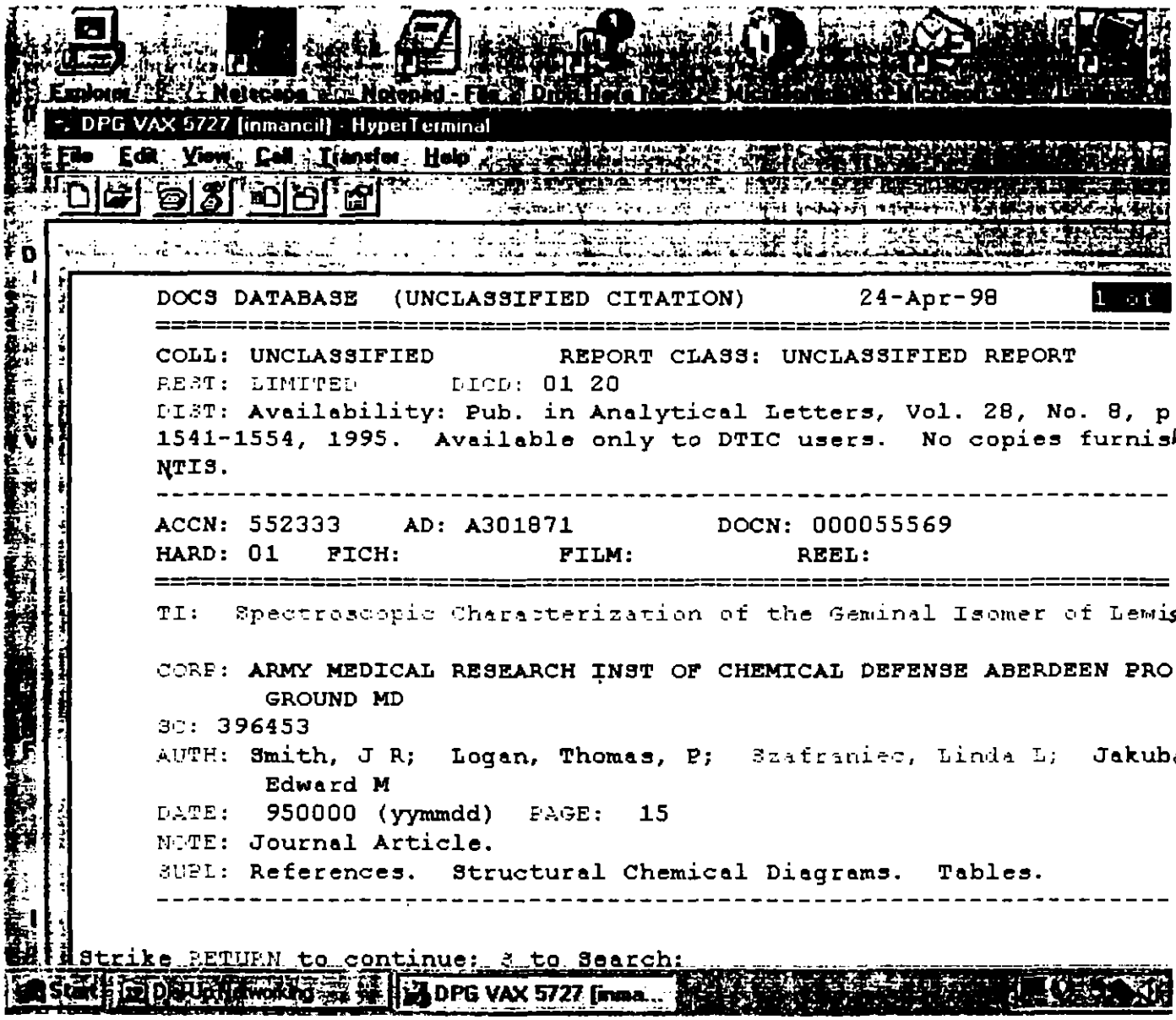
McDowell et al. calculated dipole moments for the three lewisite isomers.[2] Their calculated values were 2.03 and 1.15 Debyes for the trans and gem isomers, respectively. Two values were given for the cis isomer: 2.14 and 3.2 Debyes. The first value was based on no rotation of the $AsCl_2$ group and the second value was calculated with free rotation of the $AsCl_2$ group. Their experimental dipole moments were 2.20 and 2.61 Debyes and they assigned structures as trans and cis respectively since they were the closest to their calculated values. We re-examined the calculated dipole moments using the Spartan electronic structure molecular modeling program. The STO-3G level of theory, a relatively low level, was chosen due to its ability to handle arsenic. Our preliminary calculations indicate that the dipole moments for the trans and cis isomers are very close in value, 2.65 and 2.47 Debyes, respectively, and that the $AsCl_2$ group probably has a hindered rotation. The geminal isomer had a larger dipole moment (2.99 Debyes) than either of the stereoisomers. The closeness of the calculated values would appear to make it difficult to assign structures according to dipole moment.

In summary, we have used NMR, MS, and IR to sucessfully

characterize a previously unreported form of lewisite: a geminal isomer. Gas chromatography coupled with mass spectrometry provided a method capable of separating and identifying all three isomers in dilute solutions. The GC/IR method was able to detect and identify the gem and trans derivatives but was not sensitive enough to observe the cis derivative.

REFERENCES

1. M. Gates, J.W. Williams, and J.A. Zapp, in *Chemical Warfare Agents, and Related Chemical Problems*, National Defense Research Committee, Eds. (Summary Reports Group of the Columbia University Div. of War Research, Washington, D.C., 1946), p.83.
2. C.A. McDowell, H.G. Emblem, and E.A. Moelwyn-Hughes, *J. Chem. Soc.*, 1206 (1948).
3. J. Donohue, G. Humphrey, and V. Schomaker, *J. Am. Chem. Soc.*, 69, 1713 (1947).
4. J. Paasivirta, R. Versterinen, and L. Virkki, *Org. Magn. Reson.*, 10, 265 (1977).
5. *Systematic Identification of Chemical Warfare Agents B.3. Identification of Non-Phosphorus Warfare Agents*, Ministry for Foreign Affairs of Finland, Helsinki (1982) p.68.
6. E. Ali-Mattila, K. Siivinen, H. Kenttamaa, and P. Savolahti, *Int. J. Mass Spectrom. Ion Phys.*, 47, 371 (1983).
7. T.L. Hayes, M.I. Reeves, J.C. Arp, T.J. Chelwick, R.I. Cunningham, R.L. Zeimer, and G.S. Dill, *Proceedings of the 1989 Medical Defense Bioscience Review*, Columbia, Maryland, August 15-17, pp627-630. AD8139550
8. W.K. Fowler, D.C. Stewart, D.S. Weinberg, and E.W. Sarver, *J. Chromatogr.*, 558, 235 (1991).
9. T.P. Logan, J.R. Smith, E.M. Jakubowski, and T.W. Dolzine, *Quantitation of Lewisite Prepared in Organic Solutions Using Gas Chromatography, USAMRICD-TR-*, US Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, MD., (in press).
10. L.C. Thomas, *The Identification and Estimation of War Gases by Infra-Red Spectrophotometry. Part 1., Porton Tecnical Paper No. 256*, Porton, U.K., (1951).
11. W.W. Simons and M. Zanger, *The Sadtler Guide to NMR Spectra*, Sadtler Research Laboratories., Philadelphia, PA. (1972) p.235.
12. P.D. Bartlett, *Office of Scientific Research and Development Report No. 402, RG 227, Div. 9, Feb. 20, 1942*, Harvard University (1942) p.1.
13. S. Meyerson and A.W. Weitkamp, *Org. Mass Spectrom.*, 1, 659 (1968).
14. M. Vairamani and M. Saraswathi, *Mass Spectrom. Rev.*, 10, 491 (1992).
15. E.M. Jakubowski, J.R. Smith, T.P. Logan, N.D. Wiltshire, C.L. Woodard, R.A. Evans, and T.W. Dolzine, *Proceedings of the 1993 Medical Defense Bioscience Review*, Baltimore, Maryland, May 10-13,1993.
16. G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley and Sons, Chichester (1980) p.32.


DPG VAX 5727 [inmancil] - HyperTerminal
File Edit View Call Transfer Help
DOCS DATABASE (UNCLASSIFIED CITATION) 24-Apr-98 1 of 1
COLL: UNCLASSIFIED REPORT CLASS: UNCLASSIFIED REPORT
REST: LIMITED DICD: 01 20
DIST: Availability: Pub. in Analytical Letters, Vol. 28, No. 8, p 1541-1554, 1995. Available only to DTIC users. No copies furnished by NTIS.
ACCN: 552333 AD: A301871 DOCN: 000055569
HARD: 01 FICH: FILM: REEL:
TI: Spectroscopic Characterization of the Geminal Isomer of Lewis;
CORP: ARMY MEDICAL RESEARCH INST OF CHEMICAL DEFENSE ABERDEEN PROVING GROUND MD
SC: 396453
AUTH: Smith, J R; Logan, Thomas, P; Szafraniec, Linda L; Jakubowski Edward M
DATE: 950000 (yymmdd) PAGE: 15
NOTE: Journal Article.
SUPL: References. Structural Chemical Diagrams. Tables.
Strike RETURN to continue; ? to Search:
Start
DPG VAX 5727 [inma...

DPG VAX 5727 (inmancil) - HyperTerminal

File Edit View Call Transfer Help

REPT: USAMRICDP95002 PROG: 62787A PROJ: 3M162787A875

AB: (U) Lewisite is generally a mixture of several components with the trans isomer of lewisite being the predominant compound. A geminal isomer has not been previously reported as one of the components of the mixture. In the lewisite samples we examined, the geminal isomer dichloro(1- chlorovinyl)arsine, comprised 2.7 per cent of the total material compared to 95.2 and less than 1 per cent, respectively, for the trans and cis isomers. The remaining fraction was not identified. The geminal isomer of lewisite has been characterized along with the trans and cis isomers using several spectroscopic techniques. Proton NMR of the geminal isomer produced a coupling constant consistent with vinylic protons in a geminal configuration. Mass spectrometry and infrared spectroscopy characterizations were based on an ethanedithiol derivative of the lewisite isomers with gas chromatography used to first separate the derivatized isomers. The electron ionization mass spectra of the trans and cis derivatives were very similar, but significant differences were observed in the mass spectrum of the geminal form. Infrared absorption spectra were obtained for the trans and geminal derivatives with significant differences observed between the two, but the method was not sensitive enough to detect the cis isomer.

Strike RETURN to continue; S to Search: _

Connected 0:07:33 VT100 115200 8-N-1 SCROLL CAPS

DERIVATION OF HEALTH-BASED ENVIRONMENTAL SCREENING LEVELS FOR CHEMICAL WARFARE AGENTS

A Technical Evaluation

March 1999

Prepared by

U.S. ARMY CENTER FOR HEALTH PROMOTION AND PREVENTIVE MEDICINE
Aberdeen Proving Ground, Maryland

in conjunction with

TOXICOLOGY AND RISK ANALYSIS SECTION
LIFE SCIENCES DIVISION
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

SPECIFICALLY, THIS DOCUMENT PROVIDES GUIDANCE AND TECHNICAL REFERENCE MATERIAL BASED ON SCIENTIFIC INFORMATION CURRENT AT THE TIME OF ITS PUBLICATION. AS THIS INFORMATION AND SUPPORTING DATA ARE CONTINUOUSLY BEING ADVANCED, USERS ARE CAUTIONED TO ASCERTAIN EXISTENCE OF ANY UPDATED INFORMATION.

QUESTIONS SHOULD BE REFERRED TO:

U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM); ATTN: MCHB-TS-EHR, APG, MD, 21010-5422

POC: Ms. V. Hauschild
Phone: 410-436-2953, FAX 410-436-8170

TABLE OF CONTENTS

TABLE OF CONTENTS (cont'd)

LIST OF TABLES

LIST OF TABLES (cont'd)

ACKNOWLEDGMENTS

The authors D. Opresko *(Principle author)* and V. Hauschild *(Coauthor and Project Manager)* wish to express their appreciation to all participating individuals and organizations for their valued input to the discussions concerning the issues addressed in this report.

This report was a joint initiative of the Environmental Health Risk Assessment and Risk Communication Program, U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM), Aberdeen Proving Ground, Maryland, and the Life Sciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, under Interagency Agreement Numbers 1769-1769-A1 and 2207-M135-A1. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract No. DE-AC05-96OR22464.

Special thanks go to the other primary contributors of this document to include T. Taylor, USACHPPM; P. Selby, L. Bloom, and A. Watson of ORNL, as well as M. Major and H. Bausum of USACHPPM.

The authors gratefully acknowledge contributions of literature and guidance regarding cancer risk analysis provided by Dr. David Gaylor, Associate Director for Risk Assessment Policy and Research at the National Center for Toxicological Research, Food and Drug Administration, Jefferson, Arkansas.

Appreciation is also noted for the specific support and assistance provided by Mr. Steve Kistner and B. Gaborek as well as other USACHPPM personnel, particularly of the Environmental Health Risk Assessment and Risk Communication Program.

Reviewers of this work included staff of USACHPPM and staff of the various centers and program managers within the U.S. Army Soldier and Biological Chemical Command (SBCCOM), the US Army Environmental Center (USAEC), the U.S. Army Nuclear and Chemical Agency (USANCA), the U.S. Army Corps of Engineers (USACE; Directorate of Military Programs), and the Program Manager for Chemical Demilitarization (PMCD). The DA Steering Committee for Standards for Emergency Response, Restoration, Remediation, and Demilitarization is noted for its assistance by establishing the forum through which these organizations could collectively contribute to this document.

EXECUTIVE SUMMARY

DERIVATION OF HEALTH-BASED ENVIRONMENTAL SCREENING LEVELS FOR CHEMICAL WARFARE AGENTS

1. PURPOSE.

The purpose of this document is to evaluate currently available data and scientific methods for the assessment of potential chronic human health risks from residual chemical warfare agents in environmental media. With the identified information, associated health-based environmental screening levels (HBESLs) are then calculated. Specifically, existing U.S. Environmental Protection Agency (USEPA) chronic risk assessment methods are used with parameter assumptions defined for two common theoretical exposure scenarios to calculate a set of HBESLs for soil for the vesicant chemical warfare agents sulfur mustard (HD) and Lewisite, and the nerve agents Tabun (GA), Sarin (GB), Soman (GD) and VX. *The document is a technical reference reflecting the scientific models and data available at the time of publication. The user is cautioned to consider any scientific advances that may impact the information contained herein.*

2. APPLICATION AND LIMITATIONS.

2.1 Environmental screening levels (referred to by different names by different USEPA Regions) are low-level concentrations of individual chemicals in environmental media which, if not exceeded, are unlikely to present a human health hazard for specific exposure scenarios. Different EPA regions have used risk assessment models to establish screening levels for hundreds of industrial and agricultural chemicals that present contamination problems, and similarly, these models may be used to calculate screening levels for chemical warfare agents. During the initial evaluation phase of an environmental health risk assessment, these pre-established environmental screening levels for chemical compounds can aid the assessment process by their use as 'action or no-action' determinant criteria. For a specified scenario, if the actual soil concentrations fall below an established screening level, typically no further 'action' is deemed necessary. If concentrations are above the screening level, additional 'action' is generally required. This 'action' requirement may be met by a variety of procedures to include: performing a detailed site-specific health risk assessment; applying management controls to minimize exposure; implementing treatment/remedial operations; or a combination of these options. By focusing assessment efforts only where "action" is necessary, screening levels can help to optimize resources and minimize unnecessary expenditures of time and money. Screening levels, however, may not be appropriate for all situations. First, certain technical assumption criteria must be met, and second, all stakeholders (including specific Army activities/installations, state/local regulators, and the public) must agree to their appropriateness. *The calculated screening levels in this document are supported with the necessary documented scientific rationale; however, site-specific stakeholder input is a necessary part of their use.*

2.2 Another benefit of environmental screening levels is that they allow a means to determine

whether analytical detection capabilities for chemical contaminants are adequate. This is particularly beneficial if the compounds are very toxic and the resulting screening levels are extremely low.

2.3 Finally, in addition to the utility of the screening levels, this document provides a consolidated reference for discussion/documentation of various exposure parameters and chemical-specific environmental fate issues. *Much of the information regarding the use of a particular risk assessment model and certain input parameters can be used to facilitate site-specific risk assessments.*

3. SCOPE.

3.1 This report compares and discusses the differences and limitations of three USEPA risk assessment methods. These are the USEPA Region III Risk-Based Concentration (RBC) model, the USEPA Region IX Preliminary Remediation Goal (PRG) model, and the recently established USEPA Office of Solid Waste and Emergency Response Soil Screening Level (SSL) model. Using these methods and the Army-approved interim chronic toxicity values[1] for the chemical agents, this report calculates HBESLs for two common generic exposure scenarios (residential and commercial/industrial) that are used by the EPA and which may be used to meet screening goals for cleanups conducted at DOD/Army facilities/sites. These HBESLs address the long-term/chronic exposures to residual levels of chemical agent in the environment at such sites and are not applicable to deployed troops or acute exposures created by catastrophic chemical agent releases. Considerations regarding the potential application of chronic risk models to other scenarios, including problems with such applications, are evaluated in various appendices of this document (See appendices C and D).

3.2 Descriptions of agent HBESLs include documentation of efforts to make the most reasonable assumptions for the exposure parameters and relevant pathways associated with the residential and industrial/commercial exposure scenarios. USEPA default values are used for many of the population-, chemical-, and site-specific parameters. However, factors such as agent persistence, degradation, and dose-response relationships were carefully analyzed and non-default values incorporated into the HBESL derivation procedures. In the process of evaluating agent environmental fate and transport, the key environmental breakdown products of chemical agents were identified. Specific discussion regarding the potential for chemical agent contamination of ground water and drinking water is also presented in this document.

4. CONCLUSIONS.

4.1 The three EPA methods assessed are very similar; the differences do not generally yield substantially different screening levels. The additive pathway approach represented by PRG's generally results in some of the more conservative (lower) values, primarily due to the additive effects of the

[1] The chronic toxicity values [reference doses (RfDs)] associated with the agents are identified as "interim" by the Army and are undergoing review and evaluation by external expert panels. If the chronic toxicity values are modified as a result of this review process, the calculated HBESLs in this report may be subject to change. (DA 1996a)

inhalation route, and, to some degree, the dermal route. The SSL inhalation pathway model also produces some of the most conservative values. For the vesicants HD and L, the RBC model must be used cautiously to ensure resulting concentrations do not yield acute effects. In all, the "best" model may vary for different chemicals and situations. The benefits and disadvantages of one method over another are somewhat speculative, but depend on chemical and site/exposure-specific considerations. Ultimately, stakeholders (including site regulators, the public, and Army personnel) must evaluate the available information to determine whether the use of a screening approach is warranted and, if so, what models and parameters best suit the situation.

4.2 The HBESL values calculated in this document are intended to represent conservative values for use in *screening* contaminated sites for potential human health risks. The degree of 'conservatism' that is truly represented cannot be quantified due to the uncertainties inherent to the risk assessment models. These uncertainties are further compounded by limited data regarding both the chemical warfare agents and the human exposure process. A limitation of the application of the HBESLs for generic scenarios is that, by using a standardized approach and assumptions, unique site-specific variables may be overlooked. Therefore, before application of HBESLs as action/no-action determinants, the user must first evaluate the situation to ensure that certain assumption criteria are met. This includes ensuring that all stakeholders have input to the application of screening levels. However, despite the weaknesses associated with deriving and applying HBESLs, they provide a mechanism to make efficient, consistent, and scientifically-based action/no-action decisions when assessing the potential for chronic health effects to exposed populations.

4.3 While chemical agent residue could potentially exist in the environment for extended periods of time, it is a realistic possibility that the agents themselves will degrade/breakdown relatively rapidly. Current EPA models do not consider environmental degradation; it is therefore quite possible that actual exposure durations/frequencies are significantly overestimated resulting in conservatively 'safe' screening levels. *With the exception of HD, which under certain environmental conditions could persist for particularly extended periods of time agent after being encapsulated in an inert polymeric coating formed by its hydrolysis products, the other chemical agents described in this report would generally never persist more than a few months.* The complex issue of degradation should be considered in chemical and site-specific evaluations when using screening levels and may need to be more critically incorporated in a site-specific risk assessment. The issue of degradation, however, goes beyond the persistence of the agents themselves. In the cases of Lewisite and VX, assessments for the presence of breakdown compounds Lewisite oxide and inorganic arsenic (for Lewisite) and S-(Diisopropylaminoethyl) methylphosphonothioate (i.e. EA-2192, for VX) are warranted due to their particular toxicity and potentially significant persistence. Other likely breakdown products such as thiodiglycol from HD, and methylphosphonic acid (MPA) from the G-agents and VX, do not pose a significant health risk. However, due to their persistence in the environment, they may be useful indicators of historical chemical warfare agent presence.

4.4 It is unlikely that the chemical agents addressed in this document will contaminate ground water. Site-specific evaluations are recommended to identify those potential circumstances where potential ground-water contamination should be evaluated. It is also unlikely that these agents would contaminate a drinking water source. Site-specific assessment should be conducted only for those circumstances where contamination of a drinking water source is a realistic concern.

4.5 Other applications of these models may be an appropriate mechanism to assess other scenarios where there is potential for long-term or repeated exposures (such as for waste management or when assessing impervious contaminated surfaces). For these potential applications of chronic risk assessment models, common generic assumptions do not currently exist. Evaluating risks in these scenarios is the subject of potential future initiatives.

5. RECOMMENDATIONS.

The Table below lists HBESL values for two common generic scenarios using three current EPA chronic risk assessment methodologies, common default parameters, and chemical-specific parameters. The information in this document can be used to assist site-specific stakeholders in determining if screening levels can be used, and if so, what models and parameters best fit unique situation needs. The HBESLs can be used as action/no-action determinants ('action' meaning to perform site-specific health risk assessment; apply management controls; treat/remediate; or a combination of these) when assessing the potential for chronic health effects to exposed populations so long as the following conditions are met:

5.1 *Levels of risk are acceptable to the situation (see Section 1.3.2).*

5.2 *Assumptions made in these scenarios are at least equally conservative, if not more conservative, than site-specific values.*

5.3 *Substance concentrations and exposure assumptions are not expected to be acutely toxic (see Section 1.3.8)*

5.4 *A single chemical is of concern (see Section 1.3.9).*

5.5 *Ground-water contamination is not considered to be a concern (see Appendix E).*

5.6 *Risk to ecological receptors is not expected (see Section 1.3.10).*

Table Exec-1: Range of Estimated HBESL Values for Chemical Warfare Agents

	Residential soil (mg/kg)			Industrial soil (mg/kg)		
	RBCs	PRGs	SSLs	RBCs	PRGs	SSLs
HD	0.55	0.01[a]	0.016	14	0.3[b]	NA
Lewisite[d]	7.8	0.3	7.8	(7.8)[c]	3.7	NA
GA	3.1	2.8	1.2	82	68	NA
GB	1.6	1.3	0.5	41	32	NA
GD	0.31	0.22	0.31	8.2	5.2	NA
VX[c]	0.047	0.042	0.047	1.2	1.1	NA

[a] Cancer-based; calculated for a target risk level of 10^{-5}

[b] Cancer-based; calculated for a target risk level of 10^{-4}

[c] Assessment should include EA-2192, a particularly toxic and relatively persistent breakdown component of VX. Due to similar toxicity, the HBESLs derived for VX can be used for EA-2192.

[d] Assessment should include CVA, Lewisite oxide, and arsenic, three persistent breakdown products of Lewisite. USEPA screening levels for inorganic arsenic should be consulted. HBESLs for Lewisite can be used for Lewisite oxide.

[e] RBC value derived for the commercial/industrial scenario was potentially above acute toxicity levels, therefore the upper bound value of the residential scenario is suggested as a substitute.

1. INTRODUCTION

1.1 PURPOSE

The purpose of this document is to evaluate currently available data and scientific methods to assess the potential chronic human health risks from residual chemical warfare agents in environmental media. With the identified information, associated health-based environmental screening levels (HBESLs) are then calculated. Specifically, existing EPA chronic risk assessment methods are identified and then used with parameter assumptions for two common theoretical exposure scenarios to calculate a set of HBESLs for soil for the vesicant chemical warfare agents sulfur mustard (HD), Lewisite, and the nerve agents Tabun (GA), Sarin (GB), Soman (GD) and VX. *The document is a technical reference reflecting the general scientific models, assumptions, and data available at the time of publication. The user is cautioned to consider both site specific information as well as any scientific advances that may impact the values contained here or their application.*

1.1.1 Scope

Specifically, this report compares and discusses the differences and limitations of three U.S. Environmental Protection Agency (USEPA) risk assessment methods. These are the USEPA Region III Risk-Based Concentration (RBC) model, the USEPA Region IX Preliminary Remediation Goal (PRG) model, and the recently established USEPA Office of Solid Waste and Emergency Response (OSWER) Soil Screening Level (SSL) model. Using these methods and the Army-approved interim chronic toxicity values for the chemical agents, HBESLs for the vesicant chemical warfare agents Lewisite and HD, and the nerve agents GA, GB, GD and VX were calculated. Specifically, this document includes HBESLs for soil for two common, generic exposure scenarios: the residential scenario and the commercial/industrial. These same two scenarios are used by the EPA to establish screening levels for hundreds of industrial and agricultural chemicals. These screening levels provide for a process of a first-phase, preliminary evaluation of contaminated sites by means of identifying contaminants of concern and determining if additional evaluation is warranted[1].

Similarly, these HBESLs address the long-term/chronic exposures to residual levels of chemical warfare agent materials in the environment at potential Army environmental restoration and Formerly Used Defense (FUD) sites. In addition, potential applications and limitations of the use of these chronic risk assessment models for scenarios involving less common assumptions are discussed. In any application, there are limitations to the usefulness of these models and, in certain cases, the standard assumptions and/or the models themselves are not appropriate. Specific examples of such limitations are described.

[1]Note: As described in more detail in sections 1.1.2 and 1.2.2, screening levels should not be construed as cleanup levels.

1.1.2 Application

During the initial evaluation phase of an environmental health risk assessment, pre-established environmental screening levels for chemical compounds can aid the assessment process by their use as "action or no-action" determinant criteria. For a specified type of scenario, if the actual soil concentrations were to fall below an established screening level, no further "action" would be deemed necessary. If concentrations were above the designated screening level, additional "action" would be necessary. This "action" requirement may be met by a variety of options to include: performing a detailed site-specific health risk assessment; applying management controls to minimize exposure; implementing treatment/remedial operations; or a combination of these options. By focusing assessment efforts in this manner, screening levels can help to optimize resources and minimize unnecessary expenditures of time and money. Screening levels, however, may not be appropriate for all situations. First, certain technical assumption criteria must be met, and second, all stakeholders (e.g. state/local regulators, public and Army personnel) must agree to their appropriateness. *Given the current scientific methodology and information available, the calculated values in this document represent reasonable screening level values; however, their use requires both an understanding of the associated uncertainties and data gaps as well as site-specific stakeholder input.*

Another benefit of pre-established environmental screening levels is that they provide a means to determine whether analytical detection capabilities for chemical contaminants are adequate. This is particularly beneficial if the compounds are very toxic and the resulting screening levels are extremely low.

Finally, in addition to the utility of the pre-established screening levels established in this document, much of the information regarding the selected risk assessment model and input parameters can be used to facilitate the *site-specific* risk assessments. This document provides a consolidated reference for discussion/ documentation of various exposure parameters and chemical-specific environmental fate issues.

1.2 BACKGROUND

1.2.1 General USEPA Risk Assessment Methodology

The scientifically accepted method of assessing potential health risks from contaminated environmental media is based on the algorithm models designed and standardized by the USEPA for assessing risks at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites, also known as "Superfund" sites. The "health risks" potentially associated with such sites are independently assessed for noncarcinogenic (or "noncancer") and carcinogenic (cancer) endpoints. Noncancer risks are determined by comparing estimates of exposure to noncancer-causing chemical contaminants for multiple exposure pathways (e.g., ingestion, inhalation, and dermal contact and absorption) with toxicity values independently derived from laboratory or epidemiological data [Risk Assessment Guidance for Superfund (RAGS), USEPA, 1989b]. Noncancer toxicity values consist of oral reference doses (RfDs) and inhalation reference concentrations (RfCs). An RfD is "an estimate (with an

uncertainty spanning perhaps an order of magnitude or greater) of a daily (ingestion) exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime" (USEPA, 1989). Likewise, an RfC is an air concentration of a chemical that is not expected to produce any deleterious effects even if (inhalation) exposures continued for a lifetime (USEPA, 1994b). Excess cancer risks at a Superfund site are calculated from estimates of potential exposure and from cancer slope factors (CSFs). A CSF defines the upper bound lifetime probability of an individual developing cancer as a result of being exposed to a unit dose of the chemical. For industrial chemicals, RfDs, RfCs, and CSFs derived by USEPA are made available to the public by being incorporated into USEPA's Integrated Risk Information System (IRIS; USEPA, 1997a) or on the Superfund Health Effects Assessment Summary Tables (HEAST; USEPA, 1997c).

Actual site-specific risk assessments (sometimes referred to as baseline risk assessments) involve detailed, site-specific analyses of all potential pathway-specific exposures. Potential exposures across all likely pathways for a given chemical are summed. For noncancer endpoints, the total exposure is converted into a daily dose and compared to the chemical's RfD. For cancer endpoints, the total cancer risk associated with the daily exposure is determined using the chemical's CSF. *A baseline risk assessment incorporates as much site-specific information as possible to adequately define the likely exposure pathways, and includes such factors as current and expected uses of the site, population demographics, soil type, and environmental fate and transport analyses to assess the potential for offsite migration of the contaminants. Baseline risk assessments generally require significant time and effort to collect and validate site-specific data. They are often conducted at a site where initial screening has indicated a potential risk concern before remedial options are considered.*

1.2.2 Screening Approaches

In conducting health risk assessments at Superfund sites, a tiered approach is used in which the first step is a screening evaluation where the measured levels of environmental contamination are compared with pre-established environmental screening levels. Environmental screening levels (referred to by different names by the various USEPA Regions) are low-level concentrations of individual chemicals in environmental media, which, if not exceeded, are unlikely to present a human health hazard for specific exposure scenarios. These "low-level" concentrations are back-calculated from the USEPA risk assessment models using predetermined, conservative "acceptable risk" quantifiers. The screening approach can aid the risk assessment process by identifying those sites where either a more detailed baseline risk assessment or some other form of action (such as remediation) is necessary. However, the screening process and pre-established screening level lists vary. The screening evaluation and the final screening values are a function of the number of environmental media and exposure pathways that are included. Screening methods based on multi-media and multi-pathway analyses are intrinsically more conservative than those that are media and/or pathway-specific. The primary screening methods that have been developed by the USEPA include PRGs, RBCs, and SSLs. These methods are described in more detail below. Each USEPA regional office may support the use of one or more of these screening approaches. State regulatory agencies may require the use of specific screening methods for sites within their jurisdiction.

Preliminary Remediation Goals (PRGs). Preliminary Remediation Goals (PRGs) are described in Part B of the RAGS (USEPA, 1991a). PRGs are used at the scoping phase of the risk assessment process. The residential soil PRG given in RAGS is derived from an estimate of the potential ingestion of soil. For industrial/commercial land uses, a soil PRG is calculated based on soil ingestion, as well as inhalation of volatiles released from soil and/or inhalation of airborne particulate matter. USEPA Region IX supports the use of PRGs with the modification that skin contact and inhalation (of volatiles or particulates) are also included as components of both the residential and industrial soil PRGs (USEPA, 1996b, 1998). Region IX also has a separate pathway-specific PRG for inhalation of contaminants in ambient air. The PRG methodology requires the use of certain chemical-specific data, such as diffusivity coefficients, to calculate a volatilization factor for each chemical contaminant. A nonchemical-specific "particulate emission factor" is used for chemicals that are not volatile.

Risk-Based Concentrations (RBCs). USEPA Region III (USEPA, 1996a) supports the use of RBCs which are similar to PRGs. USEPA Region III calculates a soil ingestion RBC for noncarcinogens (for children only) and for carcinogens (age-adjusted for a 30-year exposure period), but does not include inhalation or dermal contact as additional exposure pathways for contaminated soil. However, Region III calculates a pathway-specific RBC (inhalation only) for ambient air, as well as an RBC based specifically on ingestion of edible fish.

Soil Screening Levels (SSLs). USEPA's Office of Solid Waste and Emergency Response has developed soil screening guidance which is used to derive risk-based, site-specific SSLs (USEPA, 1996c). SSLs are concentrations of contaminants in soil that would be protective for residential exposure scenarios. For contamination of surface soils, SSLs are derived for two pathways, ingestion of soil and inhalation of fugitive dusts. For subsurface soils, SSLs are also derived for two pathways, inhalation of volatiles released from the soil and ingestion of ground water contaminated as a result of the migration of chemicals through the soil to the underlying aquifer.

1.2.3 Physical/Chemical Properties and Environmental Fate of Chemical Warfare Agents

Basic chemical and physical data for agents HD, Lewisite, GA, GB, GD, and VX are given in Table 1-1. The agents discussed in this report occur as liquids at ambient temperatures; however, HD freezes at approximately 57°F and, therefore, may not behave as a liquid in temperate climates. In terms of their absolute vapor pressures, all the agents except VX are considered to be volatile; that is, transfer from a liquid to a vapor state will occur. However, in terms of their potential for volatilization from an environmental matrix (i.e., subsurface soil or water), only HD is considered to be volatile by USEPA's definition of volatility (see Section 1.3.6).

HD is reported to be slightly soluble in water, but once dissolved is subject to rapid hydrolysis. According to Small (1984) the half-life for HD is less than 16 minutes and "does not vary appreciably in the typical environmental pH range"; however, MacNaughton and Brewer (1994) state that reversible reactions take place in acidic solutions and decomposition is accelerated in neutral and basic medium. For HD in equilibrium with water, the maximum rate of hydrolysis has been reported to be 104 mg/min/L at 25°C (Forsman et al, 1979). However, the reported rate of dissolution is only 6.77×10^{8} g/cm^2/sec (Rosenblatt et al., 1975). Thus, it was reported that the half-life of a 5 µL drop of HD in stirred distilled

water at 20°C would be 250 min (Sage and Howard, 1989), and a droplet of HD 1 cm in diameter would take 15 days at 18°C to decrease by one-half (Small 1984).

The hydrolysis of Lewisite is very rapid (Rosenblatt et al., 1975). In aqueous media, Lewisite exists primarily as 2-chlorovinyl arsonous acid (CVAA) (Major, 1998). Chlorovinyl arsenous oxide (Lewisite oxide) occurs as a dehydration reaction product of CVAA. Lewisite oxide is about 1% soluble in water (Rosenblatt et al., 1975). Though there are somewhat limited toxicological data on the breakdown products, Lewisite oxide it has been suggested that the toxicological data associated with Lewisite may be more representative of it degradation products (due to the extremely rapid hydrolysis) .

The nerve agents are water soluble to varying degrees, with agent GB being miscible and the other nerve agents having solubilities ranging from 10 to 100 g/L. When dissolved in water, all the agents are subject to hydrolysis. Hydrolysis rates of the nerve agents are pH- and temperature-dependent (MacNaughton and Brewer, 1994). Data reviewed by MacNaughton and Brewer (1994) indicate that the hydrolysis of GB is slowest at pH 6-7 but much faster at higher or lower pHs. For GD, hydrolysis rates are similar over a pH range of 5-8. Because hydrolysis products may alter the pH of the solution, half-lives measured under pH-controlled laboratory conditions may not correspond to those occurring under ambient conditions. Although a half-life of >1000 hours has been reported for VX at pH 7, spontaneous half-lives of 80 and 57 hours have also been reported.

When applied to the surface of soils, the agents are generally nonpersistent. Persistence times for agents on soil are generally less than several weeks, but may be longer at low temperatures. Longer persistence times are likely when agents are buried in dry soil. Rosenblatt et al. (1995) estimated that even under the worst plausible conditions in a relatively dry but not totally water-free soil, agent GB would not be detectable after a month or less. Under similar conditions, the less volatile VX would not be detectable after about 3 months. When sprayed on soil, HD persists for several weeks (DA, 1974; Small, 1984); however, when buried in soil it may remain vesicant for several years or more (Small, 1984; Rosenblatt et al., 1995). HD buried in soil can become encapsulated in a polymeric coating formed with its hydrolysis products (Rosenblatt et al., 1995). These "capsules" are stable and nonmobile and prevent the enclosed mustard agent from undergoing further degradation. Additional information on the environmental fate of chemical warfare agents can be found in DA (1974), Small (1984), Sage and Howard (1989), MacNaughton and Brewer (1994), and Rosenblatt et al. (1995).

In summary, there are limitations with the data available to establish quantitative estimates of environmental parameters. That said, environmental fate and transport assumptions for a variety of industrial chemicals are also constrained by limited data and variability due to climate, moisture, pH, and other environmental conditions. Therefore, the fate and transport, including degradation, of chemicals in the environment is not accommodated in the existing risk assessment models described in this document. As the basic assumption of the chronic risk assessment model is that exposure to a chemical will occur over many years, potential chemical degradation in the short term may be a factor to consider when performing further analyses or assessment of the overall risk. This is especially true for the chemical agents described in this document, as they are generally not persistent. The information in Table 1-1 and the associated uncertainties with the risk model (i.e. consistent concentrations over the long-term) should therefore be incorporated into the risk management decision-making process.

Table 1-1. Physical/chemical/environmental properties of chemical warfare agents

Property	HD	L	GA	GB	GD	VX
Primary exposure pathway	vapor/ , contact	vapor/ contact	vapor/ contact	vapor	vapor	contact
Physical state	liquid	liquid	liquid	liquid	liquid	liquid
Molecular weight	159.08	207.32	162.1	140.1	182.2	267.4
Boiling point (°C)	217	190	245	158	198	298
Vapor pres. (mm Hg at 25°C)	0.11 0.165[g]	0.58[g] 0.40 (trans) 1.56 (cis)	0.07	2.94[g]	0.40	0.0007
Water solubility (g/L)	0.920 0.8[g]	0.5[c]	98 50-100[g]	miscible[g]	21 20-30[g]	30 10-50[g]
Liquid density (g/mL at 25°C)	1.27	1.88	1.08	1.09	1.02	1.0083
log Octanol-water partition coefficient (K_{ow})	1.37[a]	NA[c]	1.18[b]	0.15[b]	1.02[b]	2.09[a]
Hydrolysis half-life (hr)	0.08 (acidic) 0.065-0.26[a]	NA[c]	2 (pH 9)[g] 8.5 (pH 7) 2.5 (pH 7)[g] 7 (pH 5) 2.5 (pH 5)[g]	5 (pH 9) 0.5 (pH 9)[g] 70 (pH 7)[g] 250 (pH 6.5)[g] 47 (pH 6) 0.5(pH 5)[g]	60 (pH 10) 0.9 (pH 9)[g] 45 (pH 6.65) 40 (pH 7)[g] 40 (pH 5)[g]	~50 (pH 9)[g] 57[d] 80[h] 1000 (pH 7)[g] 2000 (pH 5)[g]
Persistence in soil	several wk[a] 1 yr+[f]	ND	1 to 1.5 days	2.5 hr to 5 days < 1 month[f]	ND	2 to 6 days < 3 months[f]

SOURCES: DA, 1974, unless otherwise noted: for most values data points are for 20-25°C

[a] Values from Small (1984); hydrolysis half-lives at 20-25°C; soil persistence for agent applied to soil surface

[b] Estimated value from Britton and Grant (1988)

[c] Not available, cannot be calculated due to rapid hydrolysis

[d] Value from Szafraniec et al. (1990); unbuffered water, when dissolved VX causes an initial increase in the pH to 9

[e] According to Rosenblatt et al. (1975), solubility data for Lewisite are meaningless because of very rapid hydrolysis, which is limited by slow rate of dissolution

[f] Value from Rosenblatt et al. (1995); for worst plausible conditions

[g] Value from MacNaughton and Brewer (1994); hydrolysis of HD limited by rates of dissolution

[h] Value from Yang et al. (1990); spontaneous hydrolysis

1.2.4 Toxicity Values

For many environmental contaminants, USEPA has derived official oral RfDs, inhalation RfCs, and oral and inhalation slope factors which are made available to risk assessors through USEPA's IRIS or HEAST (USEPA, 1997c). This has not been the case for military-unique chemicals which may also occur as environmental contaminants. However, various exposure limits for the chemical agents (see Table 1-2) have been developed by the Army (e.g. general population air values and, recently, oral RfDs) which now permit the application of chronic risk assessment models to assessing chemical agent contamination.

Table 1-2. Available reference doses, slope factors and inhalation exposure limits for chemical warfare agents

Chemical	Oral RfD[a] (mg/kg/d)	Oral Slope Factor $(mg/kg/day)^{-1}$	Inhalation Slope Factor $(mg/kg/day)^{-1}$	General Public Air Exposure Limit[d] (mg/m^3)	Inhalation RfD[e] (mg/kg/day)
HD	7×10^{-6}	7.7[b]	300[c]	1×10^{-4}	3×10^{-5}
Lewisite[g]	1×10^{-4}	-	-	3×10^{-3}	8.6×10^{-4}
GA	4×10^{-5}	-	-	3×10^{-6}	9×10^{-7}
GB	2×10^{-5}	-	-	3×10^{-6}	9×10^{-7}
GD	4×10^{-6}	-	-	1×10^{-6} [f]	3×10^{-7}
VX	6×10^{-7}	-	-	3×10^{-7} [h]	9×10^{-8}

[a] Source: DA, 1996a

[b] Geometric mean of estimated slope factors; see Section 1.2.4 of this report for derivation

[c] DA (1996a); derived from an inhalation unit risk of 8.5×10^{-2} per $\mu g/m^3$ (see USEPA, 1991b)

[d] DHHS (1988); DA (1990, 1991)

[e] Estimated from the air exposure limits using an inhalation rate of 20 m^3/day and a body weight of 70 kg

[f] Value estimated by Mioduszewski et al. (1998)

[g] The RfD for Lewisite was considered to be nonverifiable by the Strategic Environmental Research and Development Program (SERDP) Working Group; however, this value was approved as an interim value by the Office of The Surgeon General (OTSG), pending review by the Committee on Toxicology (COT).

[h] The CDC-based and current Army general population air limit is 3×10^{-6}; recent technical evaluations suggest a potential future modification. Therefore, the potentially new value of 3×10^{-7} is used here. (USACHPPM, 1998)

The Centers for Disease Control and Prevention (CDC) have evaluated occupational and general public inhalation exposure limits for the nerve agents GA, GB, VX; the mustard agents H, HD, and HT; and Lewisite (DHHS, 1988). The Army has adopted these inhalation exposure standards (DA, 1990, 1991). Recent technical evaluations have verified the validity of the G-agent air standards but have suggested that the VX general population limit should potentially be lowered by a factor of 10 (USACHPPM, 1998). In this report the lowered VX limit (3×10^{-7}) is used in place of the existing standard (3×10^{-6}) to ensure conservatism should standards be changed. This modification did not, however, significantly impact the resulting value of the screening levels. These air exposure limits are used in this report as surrogate RfCs and are converted into inhalation RfDs (RfDi) using the standard

exposure parameters of 20 m^3/day as an adult inhalation rate and 70 kg as an adult body weight. Toxicity values derived for adults are routinely used by USEPA to develop screening values for scenarios where children are the primary receptors (i.e., soil ingestion) by including adjustments in the models, and this same approach is used in this report for the chemical warfare agents.

Under the sponsorship of the Army Environmental Center at Aberdeen Proving Ground, oral RfDs were derived for HD, Lewisite, GA, GB, GD, and VX (Opresko et al., 1998; see Table 1-2). These toxicity values have undergone extensive internal and external review, including that by the multi-agency Environmental Risk Assessment Program (ERAP) of the SERDP. The agencies participating in SERDP include the U.S. Army, U.S. Navy, U.S. Air Force, U.S. Department of Energy, and the USEPA. Following approval by ERAP, the oral RfDs were submitted to the U.S. Army OTSG, and were approved as interim values by that office on June 4, 1996 (DA, 1996a). They were similarly concurred with by the CDC (DHHS, 1997). As of March 1999, these toxicity values are undergoing review by the Subcommittee on Chronic Reference Doses for Selected Chemical Warfare Agents, COT, National Research Council. The final recommendations of the COT subcommittee should be available before the end of FY 99. The RfDs used in this report, therefore, may be subject to change following the completion of the COT review.

Agent HD is considered to be a human carcinogen (IARC, 1987; NTP, 1997). In evaluating the potential carcinogenic risks associated with HD incineration, the USEPA derived an inhalation unit risk for HD using chronic animal vapor exposure data as well as a relative potency approach based on short-term carcinogenicity studies (USEPA 1991b). No long-term animal carcinogenicity studies have been conducted from which a quantitative estimate of HD potency following oral exposures can be obtained (i.e., there is no experimentally derived oral slope factor). The relative potency value calculated by USEPA (1991b) can be converted to an oral slope factor of 95 $(mg/kg/day)^{-1}$. This value was proposed as an interim slope factor for HD by OTSG (DA, 1996a). There are, however, other estimates of the HD slope factor. The relative potency Rapid Screening of Hazard (RASH) approach, as developed by Watson et al. (1989) can be used to derive an oral slope factor of 9.5 $(mg/kg/day)^{-1}$ using the current USEPA slope factor of 7.3 for benzo(a)pyrene (BaP). The RASH method has been validated as an acceptable method for estimating carcinogenic potency (Omenn et al., 1995). The carcinogenicity of HD has also been evaluated by Gaylor (1998) using several different methods (see Appendix B). In one approach, the slope factor was estimated from the relative potency value of Watson et al. (1989) and a new slope factor for BaP derived from a study by Culp et al. (1998). The resulting HD slope factor is 1.6 $(mg/kg/day)^{-1}$. If the Culp et al. (1998) slope factor for BaP is applied to USEPA's highest relative potency value for HD, the resulting slope factor is 15.6 $(mg/kg/day)^{-1}$. Gaylor (1998) also estimated HD slope factors of 5.0 and 2.6 $(mg/kg/day)^{-1}$ using linear extrapolations from benchmark doses producing forestomach hyperplasia in rats (Sasser et al., 1989a, 1989b), and a slope factor of 5.3 $(mg/kg/day)^{-1}$ using a method based on the maximum tolerated dose (Gaylor and Gold, 1995).

The different approaches described above yield HD slope factors of 1.6, 5.0, 2.6, 5.3, 15.6, 9.5, and 95 $(mg/kg/day)^{-1}$, respectively. The Shapiro-Wilk test for normality was used to evaluate the distribution of these values. The resulting normality value was 0.58007 ($p = 0.002$), indicating that these values are not distributed normally. Log transformation of the values yielded a normality value of 0.933577 and a p value of 0.601, indicating that the values are distributed log normally. Therefore, the

geometric mean of 7.7 $(mg/kg/day)^{-1}$ is considered to be the best overall measure of the slope factor for HD. It should be noted, however, that the slope factor of 95 $(mg/kg/day)^{-1}$ could be considered an outlier in the available data set (D. Gaylor, FDA, personal communication to A. Watson, ORNL, 9 June, 1998). If this value is not used in the calculation, the final geometric mean based on the remaining six values would be 5.0 $(mg/kg/day)^{-1}$. In the HBESL calculations in this report the more conservative value of 7.7 $(mg/kg/day)^{-1}$ is used.

Issues surrounding the carcinogenicity of HD and the derivation of slope factors are currently being evaluated by the COT Subcommittee on Chronic Reference Doses for Selected Chemical Warfare Agents.

Although an oral RfD was derived for Lewisite (1×10^{-4} mg/kg/day) (Opresko et al, 1998), it was the conclusion of the Strategic Environmental Research and Development Program (SERDP) Working Group that this RfD was not verifiable because of deficiencies in the available toxicity data. The Working Group recommended that the RfD for inorganic arsenic (3×10^{-4} mg/kg/day) should be used instead. Because these values are so similar and the fact that the Lewisite RfD was recommended by the Army Office of the Surgeon General (DA 1996a) for use as an interim value, the derivation of 1×10^{-4} mg/kg/day is used in this report, pending the final recommendations of the COT.

There are no epidemiological or experimental data indicating that Lewisite is carcinogenic in humans or animals; however, the Lewisite breakdown product, inorganic arsenic, is considered to be carcinogenic. Slope factors and cancer-based screening values (PRGs and SSLs) are available for inorganic arsenic (USEPA, 1998). Specific calculations for the Lewisite screening values were done using the interim RfD (noncancer). Sites where Lewisite is a potential concern should include evaluation for inorganic arsenic to include the carcinogenic effects associated with this compound.

Dermal chronic toxicity RfDs are not currently available for chemical agents, as is the case with the majority of industrial/agricultural compounds. Using the EPA Region IX method (which assesses the dermal contact pathway), oral based RfDs are converted to (or used as surrogates for) dermal RfDs where no other information is available (USEPA1996b). In this report, available data on acute dermal effects of the agents were used to modify dermal RfDs as appropriate. For example, because the standard EPA Region IX method results in a dermal Lewisite RfD of 7 µg, which is above a potential acute dermal effect level, the Lewisite screening values in this report were calculated using a dermal RfD derived from existing acute dermal toxicity data, resulting in a more conservative estimate. This was accomplished by adjusting the reported effect level of 3.5 µg (see Section 1.3.8) by a standard factor of 10 to arrive at an estimated no-effect level of 0.35 µg. Because dose-response data are not available to be certain that 0.35 µg is a no-effect level, an additional Modifying Factor of 3 was applied, resulting in a value of 0.12 µg. For a 70 kg person this is equivalent to a dermal RfD (RfD_d) of 0.0017 µg/kg body weight (0.0000017 mg/kg).

1.3 LIMITATIONS

The HBESLs calculated in this report are to be used to *screen* sites with potential health risks. Though they are considered conservative, the actual degree of conservatism will vary depending on the unique site situation to which an HBESL is being applied. A proper balance in the conservatism of assumptions and uncertainties is necessary to ensure that decision-making is conservatively safe, but not excessively so. The major potential flaws/uncertainties in the assumptions underlying the various HBESLs described in this document are discussed along with presentation of the different models and the calculated HBESLs values. In general, these "flaws" depict a fundamental problem with using standardized algorithms and assumptions -- that unique site and chemical characteristics will be overlooked. In this way, excessive over-conservatism can lead to potential unnecessary scrutiny, concern, or even remedial action at a given site. On the other hand, underconservative assumptions could potentially cause decision-makers to over-look a potential health concern. But despite this limitation, the use of HBESLs, as indicated by the referenced approaches used in this document, is the currently accepted approach in the environmental assessment and remediation field and serves a useful purpose in focusing environmental health decision-making. *For the best decision-making, however, the underlying assumptions and associated limitations must be understood before applying the HBESLs in the decision-making process.*

When an HBESL is exceeded, additional analyses should be undertaken with more site-specific data, which in most cases leads to a complete baseline risk assessment. However, before the HBESLs are even applied to make such decisions, certain criteria must first be met. An initial site evaluation is necessary to ensure that the assumptions used to derive the HBESLs are at least as, if not more, conservative than what reasonably can be expected from the site in question. Evaluation is necessary to ensure that no potential exposure pathways have been overlooked and that no unique population, chemical, or environmental factors exist that require more site-specific HBESLs. Other components of the model need to be verified for site-specific application to ensure that the designated level of risk is "acceptable" to site stakeholders; to ensure that acute concentrations are not of concern at the site; and to verify that ground-water contamination is not a realistic possibility. Furthermore, because the HBESLs are based solely on human health endpoints, additional evaluation may be necessary in order to make determinations about potential ecological effects. A more detailed discussion of these issues and other somewhat "flawed" aspects of the risk assessment models, assumptions, and screening approaches are discussed in Sections 1.3.1 through 1.3.10.

1.3.1 Exposure Scenarios

Although the HBESLs developed in this report represent a first step in the risk assessment process, they also provide a certain level of site specificity in terms of the potential exposure scenarios evaluated. As stated, two scenarios are generally addressed by USEPA: 1)residential and 2)industrial scenarios. Residential exposure scenarios are established because these result in particularly conservative values which are protective for most all other exposure situations. However, as many sites are realistically not used or going to used as residential property, the USEPA also provides screening values for industrial/commercial scenarios. While considered less conservative than the residential-based screening values, the industrial-based values still offer conservative protection for the given scenario. A

determination can be made from general site information regarding the appropriate selection of the type (industrial or residential based) of screening values to be used in the screening assessment process.

The calculation of chemical warfare agent HBESLs for both residential and industrial scenarios are demonstrated in the main body of this document. However, the Army may need to perform site specific risk assessments to determine "safe" levels of contaminants for other types of scenarios. The higher degree of variation in site-specific parameters for such scenarios makes it difficult to establish representative, yet conservative, 'screening levels'. Examples of such scenarios include: (1) trespassers (Appendix C), and (2) evaluation of potentially contaminated land being used for agricultural/grazing purposes (Appendix D). While establishment of specific screening level values for such scenarios is precluded given current data limitations, the identified appendices present discussions of the various considerations and limitations of applying the described risk assessment models to such unique situations.

Additional scenarios that are not included in this report are those involving site-specific military uses (e.g., training operations), or military or nonmilitary recreational uses (e.g., parkland, hunting and/or fishing areas). HBESLs for such scenarios may be developed in the future as the need arises. In the interim, preliminary risk assessments may be generated for these scenarios by modifying various parameters established in this document. For example, to establish the degree of acceptable contamination at military training sites, the HBESL for an industrial scenario may be "borrowed" and certain modifications made to better reflect the uniqueness of the scenario. These modifications may be necessary because of an assumption that soldiers spend more time in contact with soil than typical industrial workers due to time spent in close contact with the soil and mud during training exercises and maneuvers, and may therefore have increased skin contact, ingestion, and/or inhalation exposures. On the other hand, soldiers may not be expected to spend every workday in the field, so their exposure duration and frequency may need to be modified to reflect a more realistic scenario.

> Certain scenarios described in this document (such as trespasser) demonstrate that the chronic risk assessment model may fail to accommodate the "acute" risk from a single "hot spot" of concentrated chemical agent. In situations where the calculated HBESL is at levels which approach potential acute toxicity concerns, it may be more prudent to consider the assessment of individual hot spots to ensure that the potential of acute risk is mitigated at these higher concentration levels. Only in situations where the agent is reasonably assumed to be homogeneously adsorbed or otherwise mixed in with the matrix (e.g., possibly waste soil or even more homogenous as in liquid matrices) is the use of the risk assessment model appropriate.

1.3.2 Target Cancer Risk Levels

An HBESL derived for the only carcinogenic agent assessed, HD, was determined not only by the exposure assumptions used and by the chemical-specific CSF [which reflects the "potency" of the

chemical to cause cancer (see Section 1.2.4)], but also by the target cancer risk level (TR). The TR value in the risk assessment model reflects the increased lifetime chance of developing cancer due to exposure to the chemical of concern. In establishing screening levels, the TR represents an "acceptable" increase in the number of cancer cases in a given population. In establishing the HBESLs in this report, TRs of 10^{-5} for residential populations and 10^{-4} for industrial/commercial scenarios are used. The following paragraphs outline the justification for the values chosen.

The TRs chosen for the development of the HBESLs for HD fall within the 10^{-4} and 10^{-6} acceptable range as determined by USEPA (1991a). While the methods described in this document, namely the PRGs, SSLs, and RBCs, use a point of departure of 10^{-6} for both the residential and commercial/industrial scenarios, this is not necessarily appropriate for most chemical warfare agent-impacted sites. The USEPA has not promulgated a single acceptable level of carcinogenic risk; however, it has indicated that "for known or suspected carcinogens, acceptable exposure levels are generally concentration levels that represent an excess upper bound lifetime cancer risk to an individual of between 10^{-4} and 10^{-6}." Furthermore, there is evidence that Federal agencies have tended to use the middle and upper part of this risk range for regulatory decisions affecting the general population. In reviewing public health policy decisions, Anderson et al. (1983) found that most regulatory decisions reduced risks to near 10^{-5}. In decisions concerning hazardous waste sites where the affected geographic area is small and where population risks are presumably also small, Travis et al. (1987) found that past regulatory actions indicated that 10^{-4} was the *de minimis* risk level for these sites, with *de minimis* risk being an acceptable level that is below regulatory concern.

For residential scenarios, some states require the use of a 10^{-6} target risk goal; however, others have adopted higher acceptable risk levels for environmental standards for the general public. In California, under Proposition 65 (the Safe Drinking Water and Toxic Enforcement Act), lifetime cancer risks less than 10^{-5} are not considered significant (Pease et al., 1990). Under the Ohio Voluntary Action Program, an acceptable risk level of 10^{-5} was adopted for both single and multiple chemical exposures for residential and commercial/industrial land use (Lohner, 1997). The State of Minnesota uses a 10^{-5} lifetime cancer risk in deriving health-based limits for protection of ground water (Minnesota Rules Chapter 4717.7300). The State of Tennessee uses a 10^{-5} risk level for surface water quality criteria (Tennessee Water Quality Standards, Chapter 1200-4-3-.03). Similarly, Texas (Water Quality Standards, Section 307.6) and Virginia (9 Virginia Code 25-260-140) use 10^{-5} for surface water quality standards. For regulating inhalation exposures, the State of Maryland has codified 10^{-5} as an acceptable risk level for exposures to the chemical warfare agent HD [Title 26.11.15, Part .01 A(8)].

A TR of 10^{-5} was chosen for residential scenarios not only because it falls within the USEPA range of acceptable risk levels and is an established acceptable risk level by many states, but also for the following reasons:

- Chemical warfare agent-impacted sites are expected to be affected by a single compound, namely the agent. The screening methods used to develop the HBESLs are typically used at sites that are impacted by numerous substances.

- HD is relatively immobile in the environment.

- Exposure to chemical agent is expected to be quite limited because most chemical-agent impacted sites have restricted access.

- Analytical detection capabilities at concentrations driven by a 10^{-6} TR are questionable. Ultimately the benefits of choosing a lower TR will be lost, because the HBESL based on a TR of 10^{-6} may be lower than the detection limit for HD in an environmental medium. *It is a common problem, even when evaluating samples for industrial chemical contaminants, that analytical detection capabilities will exceed the intended health-based goal particularly in soil or 'dirty' matrices.*

A TR of 10^{-4} was chosen for industrial scenarios for the same reasons outlined above. Additionally, although a risk level of 10^{-6} is the standard default used by USEPA for deriving PRGs for industrial/commercial land use scenarios (USEPA, 1991a), occupational exposure standards have been historically set at levels corresponding to much higher risk levels. The Occupational Safety and Health Administration (OSHA) establishes exposure limits at the "lowest feasible level which is reasonably necessary or appropriate to eliminate significant risk." In general, OSHA considers 10^{-3} a threshold of significant risk (Rodricks et al., 1987; Graham, 1993), and the agency usually does not regulate lower risks because of feasibility limitations (Lohner, 1997).

In the case of benzene, the OSHA 8-hour time-weighted average (TWA) standard is 1 ppm (Title 29, Code of Federal Regulations, Part 1910). This exposure is equivalent to 3.24 mg/m^3, or 771 µg/m^3 when converted into a 24 hours/day, 7 days/week exposure. The inhalation unit risk for benzene is 8.3×10^{-6} (µg/m^3)$^{-1}$ (value from IRIS, USEPA, 1997a). Therefore, the cancer risk at the current OSHA standard is 6.4×10^{-3} [using the standard equation, Risk = Dose x Unit Risk; i.e., 771 µg/m^3 x 8.3×10^{-6} (µg/m^3)$^{-1}$]. The current OSHA standards for vinyl chloride and inorganic arsenic are 1 ppm (2.60 mg/m^3) and 10 µg/m^3, respectively; the inhalation unit risks are 8.4×10^{-5} and 4.3×10^{-3} (from IRIS or HEAST), and the resulting cancer risk levels are 5.2×10^{-2} and 1.02×10^{-2}.

Significant risk in occupational exposures must be viewed in the context of the number of individuals who may be exposed. Establishing a standard based on a one-in-one million risk when only a small number of individuals may be exposed may not be a realistic risk management decision. Furthermore, long-term exposures to HD-contaminated soil or water are unlikely at commercial/industrial sites.

Due to the reasons discussed above, TRs of 10^{-5} for residential populations and 10^{-4} for industrial/commercial scenarios were used to calculate the HBESLs. The determination of TRs for the development of screening levels requires that a single conservative value be selected for each scenario (i.e., industrial/commercial or residential). The TRs selected for development of the HD HBESLs fall within the range generally accepted as "conservative."

When using the HBESLs developed in this document, it should be noted that an acceptable risk is not a scientifically derived value. Rather, it is a judgment decision properly made by those exposed to the hazard or their designated health officials (Kelly, 1991). Therefore, while this document has used a

predetermined level of "acceptable risk," application of the carcinogenic HBESL must incur stakeholder involvement to determine whether a lower or higher level of risk is a more appropriate decision pending site-specific circumstances.

1.3.3 Potential for Chemical Agent Migration to Ground Water

The HBESL that evaluates the potential for contamination of ground water as a result of migration of a chemical through soil (OSWER-derived SSL) requires the use of a set of simplifying assumptions which may not be applicable if a chemical's distribution in soil is very localized, if it is strongly bound to soil organics or inorganics, or if its residence time in soil is relatively short (i.e., if it is subject to rapid degradation through abiotic or biological processes). In such cases the development of a generic soil SSL based on the potential for migration to ground water may not be appropriate, and site-specific HBESLs should be considered. Of the agents evaluated in this report, the nerve agents are not expected to be persistent in soils. Studies reviewed by Small (1984) indicate that 90 percent of GB applied to soil will be lost in 5 days, and a similar decrease in VX will occur in 15 days. Soil persistence time periods under worst plausible conditions were estimated to be 1 month or less for GB and 3 months or less for VX (Rosenblatt et al., 1995). Of the nerve agent degradation/breakdown products, only EA-2192 is considered to be both environmentally persistent and sufficiently toxic to be a significant ground-water contaminant (see Appendix F).

The potential for HD to contaminate ground water is extremely low because the agent, when dissolved in water, is subject to rapid hydrolysis (see Table 1-1). Furthermore, although HD may remain in soils for long periods of time, it is known to form relatively nonmobile polymeric aggregates with its hydrolysis products; therefore, migration downward through the soil to ground water is unlikely. HD has not been found in any ground-water monitoring samples; however, its more stable but much less toxic hydrolysis product, thiodiglycol, has been found in ground water.

Lewisite dissolved in water hydrolyzes almost immediately to the soluble but nonvolatile 2-chlorovinyl arsonous acid (CVAA). Lewisite oxide may then result as a product of a dehydradation reaction. Lewisite itself is not expected to be found in ground water (nor is Lewisite oxide); however, evaluation of potential ground-water contamination should consider the more soluble CVAA or secondary degradation products such as inorganic arsenic (see Appendix F) .

Because rates of degradation are not incorporated into USEPA's methodology for deriving SSLs for migration to ground water, these screening levels do not provide an accurate estimate of the risk of ground-water contamination by reactive contaminants. The potential for chemical agent migration to, and movement through, ground water was assessed using two mathematical models, VLEACH and a horizontal flow model incorporating chemical-specific rates of hydrolysis. A description of the models and the results are presented in Appendix E. The models indicate that, in general, ground-water contamination by the agents is very unlikely except under extreme circumstances (i.e., shallow aquifer and high ground-water flow). However, even for those scenarios where the agents could theoretically reach the aquifer, horizontal transport through the ground water is predicted to be only a few hundred meters or less before the agent concentrations are reduced to levels that are below acceptable drinking water HBESLs.

1.3.4 Potential for Chemical Agent Contamination of Drinking Water

As noted in the previous section, the likelihood of agents reaching ground water is very small and, consequently, the potential for contamination of drinking water derived from a ground-water source is even more remote. Agents present in surface waters as a result of runoff from contaminated soils would also be subject to hydrolysis and degradation. Hydrolysis half-lives of the nerve agents are less than 80 hours at environmental pH values. Furthermore, hydrolysis of some agents, such as GB and GD, is likely to be enhanced during standard water treatment procedures, since it has been shown experimentally that hypochlorite catalyzes the reaction (see Rosenblatt et al., 1995, for review). Drinking water contamination by stable agent degradation products may be a more appropriate consideration.

When dissolved in water, the half-life of agent HD is less than 15 minutes due to its rapid hydrolysis to thiodiglycol (see Section 1.2.3). Thiodiglycol is relatively stable in water and might be used as a marker for previous water contamination with HD. HD may, however, be persistent in surface waters if present in large amounts. This is due in part to the slow rate of dissolution of HD as well as to the possible encapsulation of HD by stable oligomeric hydrolysis products which prevent further dissolution and hydrolysis (MacNaughton and Brewer, 1994; Rosenblatt et al., 1995). HD is denser than water; therefore, undissolved agent is likely to settle to the bottom of water bodies where, if undisturbed and encapsulated, it may remain for an extended period of time.

As stated previously, Lewisite hydrolyzes rapidly to CVAA. Information was not available on the persistence of CVAA. Since Lewisite oxide is a product of dehydration reaction, it would also not be expected to be present in water. Given the rapid hydrolysis of Lewisite, it has been suggessted that its toxicity may in part be attributed to these breakdown products.

1.3.5 Breakdown Products of Environmental Concern

Environmental fate and transport processes will, to a great degree, determine the relevance of particular HBESLs for specific chemical compounds. In general, the greater the reactivity of a chemical, the less likely that it will remain for very long in the environment in an unchanged state. Soil HBESLs should be evaluated in terms of the expected soil persistence of the contaminants (see Table 1-1). For very volatile or reactive contaminants, the residence time in the soils may be so short that the potential for chronic exposures will be very low. In such cases, and particularly at sites where the contaminants have weathered over a long period of time, the presence of stable degradation products may be more relevant for health risk assessments. Several of the degradation products of the chemical agents discussed in this report are evaluated in Appendix F. The information in Appendix F is not all inclusive of the degradation products that may be found in the environment, but describes compounds that may be relatively persistent and/or believed to be significantly toxic and which may, therefore, need to be investigated at a particular site. Extensive lists of agent breakdown and degradation products under several different conditions (e.g., hydrolysis, decontamination processes, combustion, and microbial degradation), including information on toxicity and availability of toxicity values (RfDs and slope factors), are provided in DA (1988), and Munro et al. (Submitted for publication, Dec 1998). These lists should be reviewed for site-specific applicability; however, it should be emphasized that a site investigation should not involve excessive sampling and analysis for all possible degradation products since the identification of trace

amounts of nontoxic or nonpersistent chemicals would not provide any more useful information. Most degradation products of the chemical agents are less toxic than the parent compounds. Therefore, a determination of key constituents of concern should be made initially to focus the risk assessment on critical areas and to avoid being hampered by unusable or unnecessary data.

1.3.6 Volatility of Chemical Agents in Water and Soil

The potential for a chemical to volatilize from water is not solely dependent on its vapor pressure. It is also a function of the chemical's water solubility and its tendency to partition between water and air. The USEPA determines whether volatilization from water is relevant for a specific chemical by using each chemical's Henry's Law Constant (H). Henry's Law Constant is the ratio of a chemical's volatility to its water solubility. According to USEPA, a contaminant with a Henry's Law Constant less than 1×10^{-5} atm-m^3/mol and a molecular weight greater than 200 is not likely to pose an inhalation hazard as a result of volatilization from drinking water in a residential setting. Henry's Law Constants were estimated for the chemical warfare agents (see Appendix A and Table 2-3). Using these criteria, the only agent that is a potential inhalation hazard from drinking water is HD ($H = 2.4 \times 10^{5}$ atm-m^3/mol and molecular weight = 159.08). However, several of the agents have higher vapor pressures than HD. GB, in terms of its absolute vapor pressure (2.9 mm Hg), is normally considered to be more volatile than HD (vapor pressure 0.11 mm Hg). Although it is counterintuitive to think that GB in water would not be a vapor hazard, chemicals with a similar vapor pressure have also been classified by USEPA as being "nonvolatile." For example, butanol has a vapor pressure of 6.7 mm Hg, but is considered by USEPA Region IX as being "nonvolatile" for the purposes of calculating drinking water PRGs (USEPA, 1998). This is because its water solubility is quite high (63,000 mg/L) resulting in a low Henry's Law Constant of 8.81×10^{5} atm-m^3/mol. Because agent GB is miscible with water, it also has a very low estimated Henry's Law Constant (5.34×10^{-7} atm-m^3/mol), and thus also fulfills USEPA's functional definition of being relatively nonvolatile from water. Although HD might be considered potentially volatile from water, its rapid rate of hydrolysis is likely to limit such losses (see Section 1.3.4).

The Henry's Law Constant of a chemical is also used by USEPA to determine if a contaminant is a potential inhalation hazard as a result of volatilization from subsurface soils (this approach is not appropriate for surface spills). Information in the Soil Screening Guidance document (USEPA, 1996d) indicates that this method is based on the assumption that, at relatively low concentrations, chemicals in subsurface soils will partition between soil-pore water and soil-pore air, depending on their water solubility and volatility. Thus, those chemicals with a low Henry's Law Constant (less than 1×10^{5} atm-m^3/mol) are more likely to remain in soil pore water. As noted above, however, this conclusion is counterintuitive for chemicals with high vapor pressures, and its applicability to every-day soils may be questionable. Thus, there is some degree of uncertainty surrounding the assumption whether or not a chemical with both a relatively high vapor pressure and a relatively high solubility, such as GB, would represent an inhalation hazard when buried in soil. According to USEPA methods, it would not.

Although HD has an estimated Henry's Law Constant slightly greater than 1×10^{5} atm-m^3/mol, volatilization from soils is likely to be limited by its rapid hydrolysis and by the formation on its outer surface of a polymeric coating (formed with its hydrolysis products) which prevents volatilization. At a site at Aberdeen Proving Ground, where the soil is known to be heavily contaminated with HD, an

innovative biological monitoring technique has not revealed any evidence of atmospheric contamination (Rouhi, 1998).

1.3.7 Multiple Pathway Exposures

The HBESL that incorporates the greatest number of exposure pathways for a residential scenario (e.g., soil PRGs), is likely to result in the lowest screening values. The appropriateness of a multipathway HBESL is, however, dependent on several factors, including: 1) whether all exposure pathways are relevant for a given contaminant, 2) whether the same toxic endpoint occurs regardless of the exposure route, and 3) whether the appropriate toxicity values (RfD or slope factor) are available for each exposure route (or whether they can be reasonably estimated by means of route-to-route extrapolation). In situations where the target organ is different for each exposure route, it may be inappropriate to calculate a multipathway HBESL. For the systemically absorbed, cholinesterase-inhibiting nerve agents, multipathway evaluations are appropriate. In the case of the vesicants HD and Lewisite, the target organs for the various exposure pathways may not be identical if the agents are not absorbed systemically. In the case of low-level oral exposures, the toxic effect is on the lining of the gastrointestinal tract; following dermal exposures, it is on the skin; and for exposures to vapors, it is likely to be on the respiratory tract and/or the eyes and skin. The effects for each of these pathways would not be expected to be additive except possibly in the case of skin exposures by vapor or contaminated soil; but even in such situations, the same location on the skin would have to be affected. Multipathway HBESLs for HD or Lewisite are likely to result in conservative values.

1.3.8 Acute Toxicity Considerations

Care must be used in deriving HBESLs for chemical agents for relatively short-term exposures (e.g., trespasser scenario described in Appendix C of this document) to ensure that such HBESLs do not approach acutely toxic levels. The latter possibility exists because the HBESLs are derived from chronic RfDs; however, a linear dose-toxic response relationship may not exist when extrapolated to scenarios involving infrequent exposures, such as the trespasser HBESLs. The following is a summary of the available information on no-effect levels and on exposure levels associated with minimal acute toxicity. A comparison of minimum effect levels and calculated HBESLs for each chemical warfare agent is presented in Chapters 4-9 and in Appendix C.

Dermal Exposures. Only one HBESL (soil PRG) quantitatively addresses the issue of dermal exposures. For chemical warfare agents that are nonvolatile and readily absorbed through the skin (e.g., VX) or those that are vesicants (HD and Lewisite), this pathway is likely to be of great concern. For VX, as little as 0.32 mg applied to the skin may cause a toxic response. Mild signs of toxicity occurred in 1 percent of the tested individuals when this amount of pure VX was applied to the forearm (DA, 1974). A dose of 5 µg/kg (0.35 mg for a person weighing 70 kg) applied to the cheeks or earlobes resulted in signs of toxicity in about half of the tested individuals (Sim, 1962). In tests where VX was applied to polyurethane-painted steel surfaces, residual amounts of 20-40 µg VX produced toxic signs in rabbits (body weights 2.06-3.85 kg) following direct skin contact for 60 minutes; residual levels of about 10-20 µg were not toxic (Manthei et al., 1985).

For HD, human data are available on minimum effects levels for percutaneous exposures. Based on data generated at the University of Chicago Toxicology Laboratory, Landahl (1945) reported a median threshold blistering dose of 32 μg for purified H and 38 μg for Levinstein H. The data were reevaluated by Reutter and Wade (1994) who reported an ED_{50} of 33.7 μg with a slope of 2.01 for H and an ED_{50} of 38 μg for Levinstein H. Landahl (1945) also reported on the frequency of erythema in the exposed subjects. At the lowest test dose of 2.5 μg, 87 of 209 individuals exhibited erythema, and 5 of the 209 exhibited blistering. An ED_{50} of 2.8 $\mu g/cm^2$ for erythema was estimated from these data (Reutter, 1998).

Several studies have evaluated the potential hazards associated with skin contact with surfaces contaminated with HD (Manthei et al., 1983, 1986, 1988). In tests using polyurethane-painted steel plates, residual amounts of HD estimated to be as low as 20 μg were shown to be capable of causing erythema, edema, and eschar formation when the plates were applied to the clipped skin of rabbits for 60 minutes (Manthei et al., 1983). The effective dose was estimated from the initial application of 0.5 mg adjusted for a maximum 96 percent (minimum 62.2 percent) loss of agent by volatilization in controls during a 30-minute aging period prior to testing. Similarly, in studies where concrete was contaminated with HD, a residual HD level of about 20 μg was shown to cause primary skin irritation in clipped rabbits following a 60-minute contact period (Manthei et al., 1986). In a later study, Manthei et al. (1988) concluded that as little as 10 μg of HD will cause observable skin irritation in clipped rabbits after 60 minutes of direct contact. Manthei et al. (1988) also found that the clipped skin of swine was less reactive to HD than rabbit skin. However, Henry (1991) reported that rabbits were 8-10 times less sensitive than humans, and, in a review of the available toxicity data, Reutter and Wade (1994) concurred with this conclusion. Thus, the overall human and animal data indicate that HD doses of only a few micrograms (e.g., an estimated 2 μg) are likely to cause erythema in a large percentage of exposed individuals, and this dose level may even cause vesication (blistering) in some sensitive individuals. It should be noted that the dose of a few micrograms must be received in a single discrete exposure.

For GB, Grob et al. (1953) applied a 0.3 mL aqueous solution containing 6 mg GB to the forearm of a 96-kg individual. The solution was allowed to evaporate. There were no signs or symptoms of toxicity and no changes in blood cholinesterase (ChE). Grob et al. (1953) also reported that 20 mg of agent dissolved in propylene glycol and applied for 3.5 hours under a cup to the forearm caused no signs or symptoms of toxicity but did result in a 22 percent reduction in red-blood cell-ChE activity (to 78 percent of the control value).

For GA and GD, information on minimum effect levels (MELs) for percutaneous exposures was not readily available[2]. MELs were estimated by extrapolation from percutaneous LD_{50} values. For VX, the ratio of the MEL (0.32 mg) and the percutaneous LD_{50} value (10 mg) is 0.032. This same ratio can be used to estimate MELs for GA and GD. It should be noted, however, that this approach is used only to derive a rough approximation of the MELs in the absence of more specific data. The ratio approach would be expected to provide accurate estimates of MELs for agents with similar dermal dose-response curves; however, such dose-response information was not available for evaluation. For GD, the

[2]Reutter (1998) identified several references pertinent to the evaluation of the acute percutaneous toxicity of GB and GD; however, copies of these references were not provided to the authors of this report, and, because they were not readily available, could not be included in this analysis.

estimated percutaneous LD_{50} value for humans is 350 mg for bare skin (DA, 1974), and, based on the MEL/LD_{50} ratio for VX, the estimated MEL for GD is 11 mg. For GA, the percutaneous LD_{50} value for humans is 1000-1500 mg (DA, 1974), and, based on the same ratio, the estimated MEL is 32-48 mg. In comparison, Freeman et al. (1954) reported that a dose of about 5 mg GA/kg body weight (about 400 mg) applied to the skin would result in inhibition of blood cholinesterase, but would not cause clinical signs of toxicity. Therefore, the MEL estimated from the LD_{50} data appears to be a relatively conservative value.

Minimum effect levels for percutaneous exposures to liquid Lewisite were not found in the available literature. However, Landahl (1945) reported that the median threshold blistering dose in a human study was 14 µg. In addition, Landahl (1945) reported that 29 out of 93 individuals exhibited erythema at the lowest study dose of 3.5 µg. In this study, 8 of the 93 individuals exhibited blistering, suggesting that the minimum effects level may be only a few micrograms. Exposure to a vapor concentration of 200 mg/m^3 for 30 minutes causes skin lesions in humans and 1 mg/m^3 for 30 minutes causes eye lesions in rabbits (DA, 1974).

Oral Exposures. In tests on humans, single oral doses of 2-4.5 µg VX/kg produced gastrointestinal symptoms in 5 of 32 individuals (Sidell and Groff, 1974). No signs of toxicity were seen in 16 individuals receiving 1.43 µg VX/kg/day for 7 days (in four doses per day of 500 mL drinking water). Assuming a body weight of 70 kg, the total daily dose would be 100 µg in 2 L of water, or a concentration of 50 µg/L. A single oral dose of 0.022 mg GB/kg produced mild signs of toxicity in humans, and a dose as low as 0.002 mg/kg reportedly caused excessive dreaming and talking during sleep (Grob and Harvey, 1958). For a person weighing 70 kg, the latter dose equals 0.14 mg and would correspond to a drinking water concentration of 0.07 mg GB/L, assuming an ingestion rate of 2 L/day. MELs for oral exposures to GA and GD were estimated from their acute toxicity (see Appendix G) to be 2.65 and 0.63 times that of GB, respectively. The resulting MEL for GA is 0.37 mg, corresponding to 0.16 mg/L for tapwater; the resulting MEL for GD is 0.09 mg, corresponding to 0.045 mg/L.

No information is available on MELs for ingested HD in humans. In rats, a daily dose of 2.5 mg/kg (about 0.8 mg/animal) for 14 days resulted in severe damage to the gastric mucosa (Hackett et al., 1987). Rats dosed subchronically with 0.03 mg HD/kg/day (approximately 0.01 mg total dose for rats weighing 0.35 kg) exhibited no signs of toxicity in one study (Sasser et al., 1996) and only mild signs of toxicity following 13 weeks of exposure (Sasser et al., 1989a). Estimates of MELs for orally administered Lewisite in laboratory animals range from 0.07 to 2 mg/kg/day (reviewed in Opresko et al, 1998).

Inhalation Exposures. Using experimental human data from a study by Kimura et al. (1960), McNamara et al. (1973) estimated that an intravenous (i.v.) dose of 0.1 µg VX/kg would have no effect on RBC-ChE activity. For an individual weighing 70 kg and breathing 15 L/minute, this i.v. dose converts to a VX concentration x time (Ct) of 0.47 $mg\text{-}min/m^3$ (McNamara et al., 1973). In studies conducted by Bramwell et al. (1963) individuals were exposed to VX (head and neck only) to Cts of 0.6 to 6.4 $mg\text{-}min/m^3$, without respiratory protection. At Cts of 0.6-1.7 $mg\text{-}min/m^3$ (0.2-0.57 mg/m^3 for 3 min), RBC-ChE was depressed 10-22 percent; at Cts of 4.8-6.4 $mg\text{-}min/m^3$ (0.8-1.06 mg/m^3 for 6-7 min), RBC-ChE was depressed 44-70 percent. Some of the exposed individuals exhibited miosis, even with their eyes closed. Rhinorrhea occurred in 14 of the 19 tests.

Baker and Sedgwick (1996) reported that in individuals exposed to 0.5 mg GB/m³ for 30 minutes, small changes were seen in single-fiber electromyography, and some individuals exhibited miosis and mild dyspnoea. McKee and Woolcott (1949) reported that individuals exposed to 0.062 mg GB/m³ for 20 minutes per day exhibited no signs of toxicity the first three days; however, miosis appeared after the fourth day of exposure. The 1-hour no-effect level would be 0.02 mg/m³. Using the relative potency approach (see Appendix G), the equivalent concentrations for GA and GD are 0.05 mg/m³ and 0.013 mg/m³, respectively.

For HD, a Ct of 12 mg-min/m³ is considered a no-effect dose for eye irritation at ambient temperatures (McNamara et al., 1975). The maximum allowable Ct for skin effects is 5 mg-min/m³ and that for eye effects is 2 mg-min/m³ (DA, 1974, 1992). Minimum effect levels for exposure to Lewisite vapors were not found in the available literature.

1.3.9 Multiple Chemical Exposures

HBESLs are calculated for single compounds, and USEPA does not have an established method for deriving screening values for chemical mixtures. For contaminants with similar modes of action and/or identical target organs, the sum total of all exposures from such chemicals is often evaluated in the baseline risk assessment for the site. For screening assessments, several approaches may be used to evaluate multiple chemical exposures. The sum total of the concentrations of all contaminants in a specific medium (i.e., soil or water) having a similar toxic effect may be compared with the lowest HBESL for that medium. This would be a conservative approach, with a relatively large margin of safety. A second approach might be to develop a hybrid HBESL based on the relative toxicity and media concentration of each of the contaminants having a similar mode of action.

1.3.10 Ecological Impacts

The HBESLs that are currently used by USEPA do not consider potential ecological impacts. The HBESLs may or may not be protective of certain habitats and species. Further investigation of this issue may be warranted in some cases. USEPA has developed guidelines for assessing ecological risks from chemical contaminants (USEPA, 1996e). Furthermore, a method exists for deriving ecological benchmarks, similar to HBESLs, for screening sites for potential ecological effects. This method utilizes toxicological data to establish screening values that are intended to be protective of wildlife populations rather than individual organisms (Sample et al., 1996; Suter and Tsao, 1996). This method has been applied to military-unique compounds such as RDX and TNT (Talmage et al., 1999) and could also be used with the chemical warfare agents.

2. EXPOSURE ASSESSMENT

2.1 EXPOSURE SCENARIOS

HBESLs in this document have been established to generically describe different types of situations that may result in human exposure to chemical agent residue as an environmental contaminant. The generic situations include a commercial/industrial scenario and a residential scenario. The scenarios are the same standard scenarios used by the EPA in calculating their industrial/agricultural compound screening levels. These scenarios may be used to establish screening goals for cleanups conducted at Department of Defense/Army facilities/sites. Choosing the scenario that best describes a given situation/site is the first step to attributing decisions to site-specific data. For instance, the HBESL for a residential exposure scenario may be exceeded, but if the future use of the site clearly does not indicate a residential setting, then comparing contaminant concentrations for the industrial/commercial scenario may be more appropriate. Careful selection of an initial screening level can avoid delays or unnecessary expenditures. Multi-scenario HBESLs provide a quick, efficient screening tool that still offers a certain degree of site-specific information.

2.1.1 Commercial/Industrial Scenario

Following cleanup and environmental restoration activities, a site might be used for commercial or industrial businesses, at which time individuals may be exposed to residual amounts of the contaminants. The potential for exposure is highly dependent on whether the individuals come into direct contact with the soil. If development of the site involves capping the soil with an impervious material such as concrete or asphalt, then contact will be minimized. If extensive areas of surface soils remain exposed, then the potential for exposure will be greater, and if the site is subject to excavation activities, then the potential exposure will be at a maximum. Both the PRGs used by USEPA Region IX and the RBCs used by USEPA Region III include an industrial/commercial scenario for potential exposure to contaminated soil. The basic exposure pathways and parameters used by these USEPA regions will also be used here. The Soil Screening Level approach (SSL) does not include the industrial scenario.

2.1.2 Residential Scenario

The residential scenario considers two possibilities: 1) that residential populations currently living near the site might be exposed as a result of environmental transport of the contaminants offsite; and 2) that the site itself might be used as a residential development at some future time after environmental restoration activities have been completed. Because residence times at a single location may be for many years, the screening values developed for residential scenarios are designed to be very protective (i.e., 30-year exposure duration). There are unique military situations, such as on-post housing, which would include residential exposures; however, because residence times for military

personnel at a given installation are limited, it would be expected that the screening levels developed for the general public would also be protective of military dependents living near the sites.

2.1.3 Other Scenarios

The two described scenarios are the basis for general screening levels, with the residential scenario levels used most often as a "first cut" and industrial levels considered on a site-specific basis or as preliminary remediation goals (USEPA 1998). However, with limitations, there are additional applications of the chronic risk screening methodology. Other 'types' of scenarios that may require an assessment to evaluate risk associated with a chronic chemical exposure include 'trespasser' scenarios-individuals who, on occasion, unknowingly or inappropriately (often illegally) enter an area of contamination concern but where no other population is involved, and agricultural land use. These types of scenarios and potential use of the EPA models are evaluated in Appendices C and D. Where data were identified and deemed reasonable for assumptions applicable to these scenarios (i.e. trespasser scenario), the assumptions and rationale are described and example HBESLs are calculated. Where no reasonable data could be 'fit' or where a generic scenario could not be defined (such as for agricultural scenarios), a discussion of considerations and uncertainties is provided. In each scenario, the uncertainties and limitations of use of the model are discussed.

2.2 EXPOSURE PATHWAYS

For the industrial scenario, the pathways of greatest concern would be dependent on the type of work involved and the degree to which contaminated soil has been isolated from the work areas. High potential exposures from skin contact, inadvertent ingestion, and inhalation of volatiles or particulates might be expected for unprotected excavation workers at unimproved sites. In contrast, relatively low exposure, mainly from inhalation of volatiles, might occur at sites that have been largely paved over.

In a residential setting, inadvertent ingestion of soil and skin contact with soil may be significant exposure pathways, particularly for children in geographic regions with mild climates which allow for a considerable amount of time spent outside the home each day. Inhalation of volatiles and fugitive dust are also possible exposure pathways; the magnitude of the exposure by each pathway being dependent on whether the contamination is in surface or subsurface soils.

2.3 EXPOSURE PARAMETERS

The exposure scenarios and pathways discussed above require the use of various parameters that may be population-, chemical- or site-specific. Population-specific parameters are dependent on age, body size (body surface area), soil ingestion rates, and activity patterns of the individuals who may be

exposed. These factors determine the frequency and extent of the exposure. The type of soil at a site determines the amount of agent adsorbed to soil particles. Soil type also affects how strongly the soil adheres to the skin and, consequently, how much chemical is available for absorption through the skin. The physical-chemical characteristics of the compound, the area of the body exposed, and the ambient temperature also affect the rate of absorption through the skin. Physical and chemical characteristics of the individual contaminants (i.e., volatility) also determine the extent that a chemical will be transported from one environmental medium to another (i.e., from soil to air). These factors, in turn, will determine whether a specific exposure pathway is relevant in deriving environmental screening levels.

In the screening approaches discussed in this report, USEPA default values are used for many of the population-, chemical-, or site-specific parameters. These default values are those recommended by USEPA's OSWER for SSLs, USEPA Region III for RBCs, USEPA Region IX for PRGs, and by USEPA Region IV. Table 2-1 lists these values, which represent estimates of average or maximum values. For a given parameter, the 50th percentile is considered by USEPA to be the average exposure level (i.e., 50% of the population would have an inhalation rate equal to or less than the amount), and the 90th or 95th percentile is considered by USEPA to be the upper bound or "reasonable maximum exposure (RME)" (i.e., 90% or 95% of the population would have an inhalation rate equal to or less than the amount) (USEPA, 1989a). In screening assessments, USEPA uses 50th percentiles for some parameters and RMEs for others.

The following sections discuss the individual parameters (population-, chemical- and site-specific). The default values, as well as alternatives, are evaluated and a rationale is provided for the value(s) chosen for the calculations in this report. It should be noted that many of the default values used by USEPA were originally recommended in the Exposure Factors Handbook (USEPA, 1989a). The handbook has been revised and updated (USEPA, 1997d), and changes are being recommended in some of the default values, but these have not been officially adopted by the USEPA for Superfund risk assessments. There are also other sources of parameter values, including regional and state guidelines, open literature values, and defaults used by organizations such as the American Industrial Health Council (AIHC, 1994). Non-USEPA default values are generally not discussed in this report, except for those parameters that have no current USEPA-recommended default.

Table 2-1. USEPA and regional default values for risk assessment calculations

Parameter	Region III (RBCs)	Region IX (PRGs)	OSWER (SSLs)	Region IV
Body weight - adult (BW_a)	70 kg	70 kg	70 kg	
Body weight - children (BW_c)	15 kg	15 kg	15 kg	
Body weight - adolescent trespasser (BW_t)	-	-	-	45 kg
Averaging time - carcinogens (AT_c)	25,550 d	25,550 d	25,550 d	
Averaging time - noncarcinogens, residential, industrial (AT_n)	365 x ED	365 x ED	365 x ED	
Exposure frequency - residential (EF_r)	350 d/yr	350 d/yr	350 d/yr	350 d/yr
Exposure frequency - industrial (EF_i)	250 d/yr	250 d/yr	-	250 d/yr
Exposure duration - residential (ED_r) (for water contaminants)	30 yr	30 yr	30 yr	30 yr
Exposure duration - residential, child (ED_c) (for soil contaminants)	6 yr	6 yr	6 yr	6 yr
Exposure duration - industrial (ED_i)	25 yr	25 yr	-	25 yr
Exposure duration - adolescent trespasser (ED_t)	-	-	-	10 yr
Tapwater ingestion - adult (IRW_a)	2 L/d	2 L/d	2L/d	2 L/d
Tapwater ingestion - child (IRW_c)	1 L/d	1 L/d	-	1 L/d
Tapwater ingestion factor (IFW_{adj})	1.09 L-yr/ kg-d	1.1 L-yr/ kg-d	-	-
Soil ingestion - adult, residential (IRS_a)	100 mg/d	100 mg/d	-	100 mg/d
Soil ingestion - adult, industrial (IRS_i)	50* mg/d	50 mg/d	-	50-480 mg/d
Soil ingestion - child (IRS_c)	200 mg/d	200 mg/d	200 mg/d	200 mg/d
Soil ingestion factor (IFS_{adj})	114.29 mg-yr/kg-d	114 mg-yr/kg-d	114 mg-yr/kg-d	
Soil contact factor (SFS_{adj})	-	504 mg-yr/kg-d	-	-
Inhalation rate - adult (IRA_a)	20 m^3/d	20 m^3/d	-	20 m^3/d
Inhalation rate - child (IRA_c)	12 m^3/d	10 m^3/d	-	15 m^3/d
Inhalation rate - industrial (IRA_i)	-	-	-	20 m^3/d

Table 2-1. USEPA and regional default values for risk assessment calculations

Parameter	Region III (RBCs)	Region IX (PRGs)	OSWER (SSLs)	Region IV
Inhalation factor (IFA_{adj}, $InhF_{adj}$)	11.66 m^3-yr/kg-d	11 m^3-yr/kg-d	-	-
Exposed skin surface - adult (SA_a)	-	5700 cm^2	-	-
Exposed skin surface - child (SA_c)	-	2900 cm^2	-	-
Volatilization Factor for tapwater (VF_w)	0.5 L/m^3	0.5 L/m^3		-
Volatilization Factor for soil (VF_s)	chem. spec.	chem. spec.	chem. spec.	chem. spec.
Particulate Emission Factor for soil (PEF)	1.32 x 10^9 m^3/kg	1.32 x 10^9 m^3/kg	1.32 x 10^9 m^3/kg	-
Dermal Absorption Factor (ABS_{derm}) organics inorganics	-	 10% 1%	-	 1% 0.1%
GI Absorption Factor (ABS_{gi}) volatiles semivolatiles nonvolatiles	NA	NA	NA	 80% 50% 20%
Soil-to-Skin Adherence Factor - child (AF_c)	-	0.3 mg/cm^2	-	1 0 mg/cm^2 (RME)
Soil-to-Skin Adherence Factor - adult (AF_a)	-	0.08 mg/cm^2	-	

Sources: USEPA, 1996a; 1996d; 1998

[a] For industrial land use scenarios, USEPA Region III uses 0.5 as the fraction of ingested soil that is contaminated.

2.3.1 Population-Specific Parameters

2.3.1.1 Age and body weight (BW)

The USEPA default value for adult BW is 70 kg. A new default value of 71.8 kg has been proposed in the Exposure Factors Handbook (USEPA, 1997d); however, this value has not yet been adopted by the OSWER. For children 1-6 years old, the group considered by USEPA to be the most susceptible to ingestion of contaminated soil, an average BW of 16 kg is the recommended default in RAGS; however, for PRGs, RBCs and SSLs, a default value of 15 kg is used. The Exposure Factors

Handbook (USEPA, 1997d) gives age-specific BWs for children, but does not recommend a single value for children 1-6 years old.

> In this report, BWs of 70 kg for adults and 15 kg for children are used.

2.3.1.2 Averaging Time (AT_c) for Carcinogens

In the derivation of screening levels for carcinogens, USEPA uses a standard default life span of 70 years, and this USEPA value is also used in the calculations made in this report. The Exposure Factors Handbook (USEPA, 1997d) recommends that 75 years be used for the average life expectancy of the general population; however, this value has not been officially adopted by USEPA. In the screening methods discussed in this report, the averaging time for noncarcinogens is equivalent to the exposure duration (see below).

> In this report, an average life span of 70 years is used to calculate cancer risks.

2.3.1.3 Exposure time (ET), exposure duration (ED) and exposure frequency (EF)

The average daily exposure to a chemical contaminant is a function of the EF (in days per year) multiplied by the ED (in years) divided by the total number of days over which the exposure occurs. In USEPA baseline and screening risk assessments, the ED is considered to be equivalent to the averaging time for noncarcinogenic endpoints. If an exposure exceeds a minimum duration defined as chronic (i.e., 7 years according to USEPA), the potential for chronic effects, as defined by the chronic RfD, will remain regardless of the length of any subsequent nonexposure period.

The standard USEPA default used for ED for occupational exposures is 25 years and, based on a 5-day work week, the standard default for EF is 250 days/year (this value excludes the 10 working days covered by a 2-week vacation period).

> In this report, the EF and ED parameters used for occupational scenarios are 250 days/year and 25 years, respectively.

For residential scenarios, ED is determined by the number of years of occupancy at the same residence. For baseline risk assessments, the USEPA default values for residence time are 9 years for a median value and 30 years for an upper bound estimate (50th and 90th percentiles, respectively) (USEPA, 1989a). PRGs, RBCs, and SSLs are based on the upper bound estimate of 30 years. It should be noted that, in risk assessments for carcinogens, the 30-year residency period is assumed to occur from birth to age 30, and calculations of intake rates are based on time-weighted averages (TWAs). The upper bound default value for EF for a residential scenario is 350 days/year (this value excludes a 2-week per year vacation period during which time it is assumed that no exposure will occur).

> In this report, the EF and ED parameters used for residential scenarios are 350 days/year and 30 years, respectively.

2.3.1.4 Skin contact with contaminated soil (SA)

For exposures that may occur as a result of skin contact with contaminated soil, the magnitude of exposure is dependent on the amount of skin surface area exposed. The area of skin exposed is a function of the age, body size, clothing worn, and activity pattern of the individual. Thus, for specific scenarios only certain body parts may be exposed (body part surface areas are given in Table 2-2). USEPA has suggested that for most soil contact scenarios for adults, the hands, lower legs, forearms, neck and head would be exposed and that the exposure would be equivalent to 25% of the total body surface area (USEPA, 1992). The default values *currently* used by USEPA Region IX (USEPA 1998) are 5700 cm^2 for adults and 2900 cm^2 for children. Body surface area estimates for children 2-10 years old are shown in Table 2-2.

> In this report, exposed skin surface areas of 5700 cm^2 for adults and 2900 cm^2 for children are used.

Table 2-2. Body surface areas for 50th percentile of population (m^2)

Age (yr)	Total body		Body part surface area for males					
	Male	Female	Arms	Hands	Legs	Feet	Head	Trunk
2 < 3	0.603 (6030 cm^2)	0.579 (5790 cm^2)						
3 < 4	0.664 (6640 cm^2)	0.649 (6490 cm^2)	0.096 (960 cm^2)	0.040 (400 cm^2)	0.18 (1800 cm^2)			
4 < 5	0.731 (7310 cm^2)	0.706 (7060 cm^2)						
5 < 6	0.793 (7930 cm^2)	0.779 (7790 cm^2)						
2 < 6	0.698 (6980 cm^2)	0.678 (6780 cm^2)						
2 < 6	0.688 (6880 cm^2)							
3 < 10	0.866[a] (8660 cm^2)	0.851[a] (8510 cm^2)	0.116[b] (1160 cm^2)	0.047[b] (470 cm^2)	0.239[b] (2390 cm^2)	0.0627[b] (627 cm^2)	0.114[b] (1140 cm^2)	0.287[b] (2870 cm^2)
Adult	1.94 (19,400 cm^2)	1.69 (16,900 cm^2)	0.228[c] (2280 cm^2)	0.084[c] (840 cm^2)	0.505[c] (5050 cm^2)	0.112[c] (1120 cm^2)	0.118[c] (1180 cm^2)	0.569[c] (5690 cm^2)

Sources: USEPA, 1989a, 1989b, 1992

[a]Calculated as an average of the median values for four age groups as given in USEPA, 1989a
[b]Calculated from the percentage of total body surface area for each body part
[c]Mean values (USEPA, 1989a)

2.3.1.5 Soil ingestion rates (IR)

Total exposures resulting from ingestion of soil are dependent on age-specific ingestion rates, EF and ED, and on the fraction of soil ingested from the contaminated source.

Children 1-6 years old are the group most susceptible to ingestion of soil (USEPA, 1989a). For this group, 200 mg/day is considered a typical soil consumption rate (50th percentile) and 800 mg/day is a "reasonable worst-case value" (90th percentile) (USEPA, 1989a). The default value used for PRGs, RBCs, and SSLs is 200 mg/day for children 1-6 years old. The new Exposure Factors Handbook

(USEPA, 1997d) recommends a new mean value of 100 mg/day, and an upper percentile value of 400 mg/day; however, these values have not yet been adopted by USEPA.

Although information on soil ingestion rates for individuals over 6 years old is very limited (USEPA, 1989a), the default value used for PRGs, RBCs, and SSLs is 100 mg/day. The new Exposure Factors Handbook (USEPA, 1997d) recommends an adult soil ingestion default value of 50 mg/day.

Another factor that may be included or incorporated into the soil ingestion rate is the fraction of soil ingested (FS) that is contaminated. The fraction of soil ingested from a contaminated source is dependent on the activity patterns of the individuals who may be exposed. Children may come in contact with the contaminated soil in their residential neighborhood, but perhaps not with contaminated soil at school, or just the opposite scenario may occur. For screening level calculations, the assumption is made that for residential exposures, all of the soil ingested comes from the contaminated source. For occupational exposures, USEPA Region III uses the assumption that the fraction of soil ingested from the contaminated source is 0.5. Applied to an ingestion rate of 100 mg/day, this results in a daily intake 50 mg/day (USEPA, 1996a). USEPA Region IX uses an occupational soil ingestion rate of 50 mg/day without incorporating a FS value (USEPA, 1998). Though the value of 50mg/day is a default value for the occupational scenario, available data (USEPA, 1997d) suggests that for very specific occupational exposures, such as excavation workers, higher defaults for soil ingestion may be appropriate.

It is also a consideration that exposure frequency for the soil ingestion pathway depends on the number of days during which soil ingestion may occur, and this, in turn, depends on climate and individual behavior patterns. USEPA has estimated that "ingestion of contaminated soil could occur typically 75% of the time over a 3-year period. In a "reasonable worst-case," this would occur 100 percent over a 6-year period" (USEPA, 1989a). USEPA exposure frequency defaults are 40-350 events per year (central and upper bound estimates). The latter value presumably would be appropriate in tropical or subtropical regions where children may be outdoors year round.

> In this report, the assumption is that 100% of soil ingested by a child is contaminated, resulting in a total contaminated soil ingestion rate of 200 mg/day. For residential adults the rate is 100mg/day. For occupational exposures, the amount of contaminated soil ingested is assumed to be 50 mg/day.

2.3.1.6 Inhalation rates (IR)

The standard USEPA default for inhalation rate is 20 m^3 per day for adults. The new Exposure Factors Handbook (USEPA, 1997d) recommends an inhalation default value of 15.2 m^3 per day for adult men and 11.3 m^3 per day for adult women; a single general population value is not given. USEPA Region III uses an inhalation rate of 12 m^3/day for children, whereas Region IX uses an inhalation rate of 10 m^3/day for children. The Exposure Factors Handbook recommends age-specific inhalation rates for children: 6.8 m^3/day for 1-2 year olds; 8.3 m^3/day for 3-5 year olds; and 10 m^3/day for 6-9 year olds.

> In this report, an inhalation rate of 20 m^3 is used adults and 10 m^3 /day is used for children.

2.3.2 Chemical-Specific Parameters

Chemical-specific parameters used in deriving HBESLs for the chemical warfare agents are listed in Table 2-3. Several of these parameters are discussed in more detail in the following sections.

2.3.2.1 Gastrointestinal absorption factor (ABS_{gi})

Gastrointestinal absorption factors (ABS_{gi}) are used to estimate a dermal RfD from an oral RfD. The dermal RfD is then compared with estimated exposures through skin contact with contaminated soil. Gastrointestinal absorptions factors are not readily available for many compounds, and USEPA Region IX allows the use of oral toxicity values (RfDs and slope factors) in place of estimates of dermal toxicity values. USEPA Region IV recommends using default gastrointestinal absorption values of 80% for volatile organics, 50% for semivolatile organics, and 20% for inorganics (USEPA, 1995b). USEPA Region IV does not provide guidance for differentiating between volatile and semivolatile organic compounds.

> In this report, oral toxicity values are used for dermal pathways except for Lewisite, where available dermal toxicity data were used to establish a more appropriate dermal toxicity value [discussed in detail in the Lewisite chapter (Chapter 9) and in section 1.2].

Table 2-3. Chemical/environmental parameters for chemical agents

Parameter	HD	L	GA	GB	GD	VX
Vapor pres. (mm Hg at 25°C)	0.11	0.58	0.07	2.9	0.40	0.0007
Solubility (g/L)	0.920	0.5	98	miscible	21	10 - 50[i]
Henry's Law Constant (H) (atm·m³/mol)	2.1×10^{-5} [a]	3.2×10^{-4} [g]	1.5×10^{-7} [g]	5.34×10^{-7} [a]	4.56×10^{-6} [g]	3.5×10^{-9} [a]
Dimensionless Henry's Law Constant (H')[f]	8.6×10^{-4}	1.3×10^{-2}	6.15×10^{-6}	2.2×10^{-5}	1.87×10^{-4}	1.43×10^{-7}
Liquid density (g/mL at 25°C)	1.27	1.88	1.08	1.09	1.02	1.0083
Air diffusivity (cm²/s)	0.099	0.099	0.092	0.10	0.082	0.062
Water diffusivity (cm²/s)	8.4×10^{-6}	9.0×10^{-6}	7.5×10^{-6}	8.2×10^{-6}	6.8×10^{-6}	5.3×10^{-6}
Apparent diffusivity (cm²/s)	5.0×10^{-6}	NA[h]	2.35×10^{-7}	5.4×10^{-7}	5.57×10^{-7}	1.7×10^{-8}
Volatilization factor (m³/kg)	5.62×10^{4}	NA[h]	2.6×10^{5}	1.7×10^{5}	1.7×10^{5}	9.67×10^{5}
Soil saturation limit (mg/kg)	460	NA[h]	32,438	-	31,585	6500
log K_{ow}	1.37[a]	NA[h]	0.384[b]	0.299[b]	1.82[b]	2.09[a]
log K_{oc}[d]	2.12	NA[h]	1.59	1.54	2.37	2.51
K_{oc}	133	NA[h]	38.5	34.6	234	327
K_d[e]	0.798	NA[h]	0.231	0.208	1.404	1.962

SOURCES: DA, 1974, unless otherwise noted: for most values data points are for 20-25°C

[a] Value from Small, 1984

[b] Experimental value; see Appendix H

[c] Due to rapid hydrolysis, water solubility data are virtually meaningless (Rosenblatt et al., 1975)

[d] Estimated using the regression equation: $\log K_{oc} = 1.377 + 0.544 \log K_{ow}$ (see Lyman et al., 1982, Equation 4-8).

[e] $K_d = K_{oc} \times f_{oc}$, where f_{oc} = organic carbon in soil (0.006 g/g, USEPA Region IX default for PRGs)

[f] H' = 41 x Henry's Law Constant (USEPA, 1996)

[g] H = H* x RT; H* = ratio of the volatility and solubility; R = gas constant (8.2×10^{5} atm·m³/mol·K); and T = temperature in K (20°C = 293.15°K)

[h] Cannot be calculated due to rapid degradation

[i] MacNaughton and Brewer, 1994

2.3.2.2 Dermal absorption factor (ABS_{derm})

The dermal absorption factor (ABS_{derm}) is a chemical-specific value which allows for the estimation of the absorbed dose. A default value for skin absorption has not been adopted agency-wide by USEPA. The Soil Screening Guidance Document (USEPA, 1996c) indicates that absorption via the dermal route must be greater than 10% to equal or exceed ingestion exposures (assuming 100% absorption of the chemical via the gastro-intestinal tract). Of 110 compounds evaluated by USEPA, only pentachlorophenol had a dermal absorption greater than 10%. However, it was also reported that certain semivolatile organic compounds such as BaP may be of concern through this exposure route (USEPA, 1996c).

For volatile organics such as benzene and 1,1-dichloroethane and other compounds having a vapor pressure similar to or greater than that of benzene (i.e., 95.2 mm Hg), USEPA Region III recommends using a default skin absorption factor of 0.05% (USEPA, 1995a). For volatile compounds with a lower vapor pressure, USEPA Region III recommends a default of 3%. Region III recommends a default value of 10% for semivolatile organics, and gives BaP as an example; however, the vapor pressure of BaP is only 5×10^{-9} mm Hg, indicating a very low potential for volatilization. For calculating PRGs, USEPA Region IX uses a default value of 10% for organics and 1% for inorganics (with the exception that an absorption factor of 3% is used for inorganic arsenic) (USEPA, 1998).

Although experimental data indicate that the skin absorption rates for many semivolatile organic compounds range from 1-10% for the pure compound, much lower absorption rates are likely to occur when the chemical is bound to soil particles. For this reason, USEPA Region IV recommends 1% as the default for organic compounds and 0.1% for inorganics (USEPA, 1995b).

Dermal absorption data for the chemical warfare agents are listed in Table 2-4. Absorption of pure agent VX on the forearm and cheek ranged from about 2 to 20% in tests conducted at 18°C (Craig et al., 1977). Lower values would be expected for the more volatile G agents, as shown by a skin absorption rate of less than 1% for the volatile nerve agent GB (Marzulli and Williams, 1953).

Based on soil partitioning coefficients, water solubility and flux across the skin, Major (1998) estimated the theoretical rates of dermal absorption of agents HD, GA, GD, GB, and VX from a soil matrix (see Appendix H). Because the HBESL exposure scenarios focus on dermal contact with contaminated soil, the ABS_{derm} values calculated by Major are used in this report. Because dermal absorption is possible until the soil is removed from the skin, cumulative absorption rates are used in the HBESL calculations. It was conservatively assumed that for a residential scenario the soil might remain on the skin for as long as 12 hours. For the commercial/industrial scenario an 8-hour cumulative absorption was used to coincide with the 8-hour occupational exposure duration.

An experimentally-derived ABS_{derm} was not available for Lewisite; therefore, a default value of 0.1 is used in accordance with USEPA Region IX guidelines for organic compounds (USEPA 1998).

Table 2-4. Dermal absorption values for chemical agents

ABS_{derm} values used in this report for soil-bound agents are:

Agent	Residential	Commercial/industrial
HD	8.4%/12 hr	5.6%/8 hr
Lewisite	10%/day	10%/day
GA	3.1%/12 hr	2.1%/8 hr
GB	4.2%/12 hr	2.8%/8 hr
GD	9.4%/12 hr	6.1%/8 hr
VX	3.3%/12 hr	2.2%/8 hr

2.3.2.3 Volatilization factor for soil (VF_s)

Volatilization of a chemical from soil is a function of the concentration of the chemical, the density of the soil particles, and the rate of diffusion of the chemical from the soil to air. Appendix A provides an equation for deriving the VF_s for each chemical agent. Derivation of the diffusion coefficient for each agent requires five chemical-specific parameters: Henry's Law Constant, diffusivity coefficient for air, diffusivity coefficient for water, soil-water partition coefficient, and soil organic carbon-water partition coefficient. The values for these parameters for each chemical agent are calculated in Appendix A and listed in Table 2-3. They are discussed further in the following sections. If a chemical is not volatile by the USEPA's definition of volatility, volatilization is not considered a potential exposure pathway; however, in the derivation of screening values the VF_s is replaced with a Particulate Emission Factor (PEF, see Section 2.3.3.2) which takes into account the possibility that exposures may occur as a result of inhalation of contaminated airborne particles.

Henry's Law Constant (H). This constant is a ratio of the volatility of a chemical to its water solubility, and thus is a measure of the tendency of a chemical to volatilize from water. Henry's Law Constants can be determined experimentally or estimated from the vapor pressure and water solubility of the chemical. Methods for estimating Henry's Law Constants for the chemical warfare agents are given in Appendix A. Henry's Law Constants for the chemical agents are listed in Table 2-3. As recommended by USEPA, the Henry's Law Constant was used not only to calculate the VF_s for each agent, but also to determine whether volatilization would be a significant exposure pathway. According to USEPA, chemicals having an H value of greater than 1×10^{-5} atm-m^3/mol and a molecular weight of less than 200 are likely to represent an inhalation hazard as a result of volatilization from water or soil. Based on this

definition, only HD is considered to be sufficiently volatile to require the inclusion of the inhalation pathway in the exposure assessment.

> Based on USEPA's definition of volatility, only HD is considered to be subject to volatilization from soil.

Diffusivity in Air (D_i). This coefficient is a measure of the tendency of a chemical to diffuse through air. It can be determined experimentally or estimated from information on the molecular weight and liquid density of a chemical. Derivations of the air diffusivity coefficients for the chemical warfare agents are given in Appendix A and listed in Table 2-3.

Diffusivity in Water (D_w). This coefficient is a measure of the tendency of a chemical to diffuse through water. It can be determined experimentally or estimated from the molar volume of a chemical. Derivations of the water diffusivity coefficients for the chemical warfare agents are given in Appendix A and listed in Table 2-3.

Soil Organic Carbon-Water Partition Coefficient (K_{oc}). This coefficient is a measure of the tendency of a chemical to partition between water and soil organics. The K_{oc} can be derived from a chemical's octanol-water partition coefficient (K_{ow}) using the following equation (see Lyman et al., 1982).

$$\log K_{oc} = 1.377 + \log K_{ow} \qquad (2\text{-}1)$$

Chemical-specific K_{ow} values were obtained from the available literature (see Table 2-3). K_{oc} values for the chemical warfare agents were derived from K_{ow} values using Equation 2-1 and are also listed in Table 2-3.

Soil-Water Partition Coefficient (K_d). This coefficient is a measure of the tendency of a chemical to bind to soils. It is derived by multiplying the soil organic carbon-water partition coefficient (K_{oc}) by the fraction of organic carbon in the soil (f_{oc}).

$$K_d = K_{oc} \times f_{oc} \qquad (2\text{-}2)$$

The default f_{oc} used by OSWER (for inhalation of volatiles), as well as by USEPA Region IX for calculating apparent diffusivities, is 0.006 g/g. K_d values for the chemical warfare agents, as derived from Equation 2-2, are presented in Table 2-3.

2.3.2.4 Soil saturation limit (C_{sat})

The soil saturation limit (C_{sat}) of a chemical is used to determine the concentration of a chemical in soil below which volatilization is a function of the solubility, volatility, and diffusivity of the chemical. Above this limit the chemical will also exist in soil in the pure undissolved state. Screening levels incorporating a volatilization factor are not accurate for chemical concentrations in soil above the C_{sat}. The equation for deriving C_{sat} values is given in Appendix A. Soil saturation limits for the chemical agents are listed in Table 2-3.

2.3.3 Site-Specific Parameters

2.3.3.1 Soil-to-skin adherence factor (AF)

The type of soil at a given site determines the soil-to-skin adherence factor (AF). In the absence of site-specific data, the Superfund Guidance Document recommends using the following default values: 1.45 mg/cm^2 for commercial potting soil and 2.77 mg/cm^2 for kaolin clay (USEPA, 1989b). USEPA (1992) has more recently reported that "a range of values from 0.2 mg/cm^2 to 1.5 mg/cm^2 per event appear possible." Based on the recently developed Dermal Exposure Guidelines, USEPA Region IX now uses a soil adherence value of 0.08 mg/cm^2 for PRG calculations for adults and 0.3 mg/cm^2 for children (USEPA, 1998). Because the USEPA Region IX approach is the one that is most commonly used, the same defaults will be used in this report.

> In this report, a soil-to-skin adherence factor of 0.08 mg/cm^2 is used for adults and 0.3 mg/cm^2 is used for children.

2.3.3.2 Particulate emission factor (PEF)

Inhalation of fugitive dusts is an exposure pathway that is considered in deriving PRGs and SSLs. Since the screening level derived for ingestion of soil is usually several orders of magnitude lower than the fugitive dust pathway, the fugitive dust pathway does not need to be routinely considered for organic chemicals in surface soils (USEPA, 1996c). Derivation of a fugitive dust SSL requires calculation of a PEF that relates the concentration of the chemical in soil to its concentration in dust particles in air. The PEF represents an annual average emission rate based on wind erosion. Derivation of the PEF is given in Appendix A. The default PEF used by USEPA is 1.32 x 10^9 m^3/kg (USEPA, 1998).

> In this report, a default PEF of 1.32 x 10^9 m^3/kg is used.

3. METHODS FOR DERIVING ENVIRONMENTAL SCREENING LEVELS

This chapter describes the equations for calculating Risk-Based Concentrations (RBCs), Preliminary Remediation Goals (PRGs), and Soil Screening Levels (SSLs).

3.1 RISK-BASED CONCENTRATIONS (RBCs)

Risk-based concentrations have been developed by USEPA Region III (USEPA, 1996a). Current EPA Region III models are used to estimate RBCs for exposure to residential tapwater, ambient air, consumption of edible fish, and residential and industrial soils. For the chemical warfare agents, RBCs are estimated in this report only for residential and industrial soil. The parameters used in the RBC equations are listed in Table 3-1. The abbreviations are those used by USEPA Region III (USEPA, 1996a).

3.1.1 RBC for Residential Soil - Noncancer Endpoint. A residential soil RBC for a noncancer endpoint for residential soil is derived using the following equation (USEPA, 1996a):

$$RBC_s = \frac{THQ \times RfDo \times BWc \times ATn}{EFr \times EDc \times \left(\frac{IRSc}{10^6\ mg/kg}\right) \times FC} \qquad (3\text{-}1)$$

3.1.2 RBC for Residential Soil - Cancer Endpoint. A residential soil RBC for a cancer endpoint can be estimated using the following formula (USEPA, 1996a):

$$RBC_s = \frac{TR \times ATc}{EFr \times \left(\frac{IFSadj}{10^6\ mg/kg}\right) \times FC \times CPSo} \qquad (3\text{-}2)$$

3.1.3 RBC for Industrial Soil - Noncancer Endpoint. An industrial soil RBC for a noncancer endpoint can be estimated using the following formula (USEPA, 1996a):

$$RBC_{is} = \frac{THQ \times RfDo \times BWa \times ATn}{EFi \times EDi \times \left(\frac{IRSa}{10^6\ mg/kg}\right) \times FC} \qquad (3\text{-}3)$$

3.1.4 RBC for Industrial Soil - Cancer Endpoint. An industrial soil RBC for a cancer endpoint can be estimated using the following formula (USEPA, 1996a):

$$RBC_{is} = \frac{TR \times BWa \times ATc}{EFi \times EDi \times \left(\frac{IRSa}{10^6\ mg/kg}\right) \times FC \times CPSo} \qquad (3\text{-}4)$$

Table 3-1. Parameters used in Risk-Based Concentration (RBC) equations

Abbrev.	Definition	Value
RBCrs	Risk-Based Concentration for residential soil	mg chemical/kg soil
RBCis	Risk-Based Concentration for industrial soil	mg chemical/kg soil
THQ	Toxicity Hazard Quotient	1
TR	Target Cancer Risk	10^{-5} (residential) 10^{-4} (industrial)
RfDo	Oral Reference Dose	mg chemical/kg body weight/day (Table 1-2)
RfDi	Inhalation Reference Dose	mg chemical/kg body weight/day (Table 1-2)
CPSi	Cancer slope factor, inhalation	$(mg/kg/day)^{-1}$ (Table 1-2)
CPSo	Cancer slope factor, oral	$(mg/kg/day)^{-1}$ (Table 1-2)
BWa	Body weight, adult	70 kg
BWc	Body weight, child	15 kg
ATn	Averaging time for noncancer effects	ED x 365 days
ATc	Averaging time for cancer effects	70 yr x 365 days/yr
K	Volatilization constant for water	0.5 L/m^3
IRAa	Inhalation rate, adult	20 m^3/day
IFAadj	Inhalation factor, age-adjusted	11.66 $m^3 \cdot yr/kg \cdot days$
IFSadj	Soil ingestion factor, age-adjusted	114.29 $mg \cdot yr/kg \cdot days$
IRSc	Soil ingestion rate, child	200 mg/day
IRSa	Soil ingestion rate, adult	100 mg/day

FC	Fraction ingested from contaminated source	100% for residential 50% for industrial
EDr	Exposure duration, residential	30 yr
EDc	Exposure duration, child	6 yr
EDi	Exposure duration industrial	25 yr
EFr	Exposure frequency, residential	350 days/yr
EFi	Exposure frequency, industrial	250 days/yr

SOURCE: derived from USEPA 1996a, with modifications

3.2 PRELIMINARY REMEDIATION GOALS (PRGs)

Preliminary remediation goals were originally developed as part of the Risk Assessment Guidance for Superfund (USEPA, 1991a). The PRG method has been adopted by USEPA Region IX (USEPA, 1996b). Region IX models are currently used establish PRGs for exposure to residential tapwater, residential and industrial soil, and ambient air. For the chemical warfare agents discussed in this report PRG models are used to calculate screening levels only for residential and industrial soil. The parameters used in the PRG equations are listed in Table 3-2. The abbreviations for these parameters are those used by USEPA Region IX (USEPA, 1996b).

3.2.1 PRG for Residential Soil - Noncancer Endpoint. A PRG for volatile or semivolatile chemical contaminants in residential soil can be estimated using the following USEPA Region IX equation (USEPA, 1996b):

$$PRG_{rs} = \frac{THQ \times BW_c \times AT_n}{EF_r \times ED_c \times \left(\left(\frac{1}{RfD_o} \times \frac{IRS_c}{10^6\ mg/kg}\right)+\left(\frac{1}{RfD_o} \times \frac{SA_c \times AF \times ABS}{10^6\ mg/kg}\right)+\left(\frac{1}{RfD_i} \times \frac{IRA_c}{VF_s}\right)\right)} \quad (3\text{-}5)$$

3.2.4 PRG for Residential Soil - Cancer Endpoint. The cancer-based PRG for residential soil can be estimated from the following USEPA Region IX equation (USEPA, 1996b):

$$PRG_{rs} = \frac{TR \times AT_c}{EF_r \times \left(\left(\frac{IFS_{adj} \times CSF_o}{10^6\ mg/kg}\right) + \left(\frac{SFS_{adj} \times ABS \times CSF_o}{10^6\ mg/kg}\right) + \left(\frac{InhF_{adj} \times CSF_i}{VF_s}\right)\right)} \quad (3\text{-}6)$$

3.2.5 PRG for Industrial Soil - Noncancer Endpoint. A PRG for a noncancer endpoint for volatile or semivolatile chemical contaminants in industrial soil can be estimated using the following USEPA Region IX equation (USEPA, 1996b):

$$PRG_{is} = \frac{THQ \times BW_a \times AT_n}{EF_i \times ED_i \times \left(\left(\frac{1}{RfD_o} \times \frac{IRS_i}{10^6\ mg/kg}\right)+\left(\frac{1}{RfD_o} \times \frac{SA_a \times AF \times ABS}{10^6\ mg/kg}\right)+\left(\frac{1}{RfD_i} \times \frac{IRA_a}{VF_s}\right)\right)} \quad (3\text{-}7)$$

3.2.6 PRG for Industrial Soil - Cancer Endpoint. A PRG for a cancer endpoint for volatile or semivolatile chemical contaminants in industrial soil can be estimated using the following USEPA Region IX equation USEPA, 1996b):

$$PRG_{is} = \frac{TR \times BW_a \times AT_c}{EF_i \times ED_i \times \left(\left(\frac{IRS_i \times CSF_o}{10^6\ mg/kg}\right) + \left(\frac{SA_a \times AF \times ABS \times CSF_o}{10^6\ mg/kg}\right) + \left(\frac{IRA_a \times CSF_i}{VF_s}\right)\right)} \quad (3\text{-}8)$$

Note: In Equations 3-7 and 3-8, the soil ingestion rate (SAa) of 50 mg/day incorporates the fraction of soil ingested from the contaminated site (50%), and the inhalation rate (IRAa) of 10 m^3/day is for an 8-hour work day; therefore, an adjustment for fraction of the day at the site is not needed.

Table 3-2. Parameters used in equations for Preliminary Remediation Goals (PRGs)

Abbrev.	Definition	Value
PRG_{rs}	Preliminary Remediation Goal for residential soil	mg chemical/kg soil
PRG_{is}	Preliminary Remediation Goal for industrial soil	mg chemical/kg soil
THQ	Toxicity Hazard Quotient	1
TR	Target Cancer Risk	10^{-5} (residential) 10^{-4} (industrial)
RfD_o	Oral Reference Dose	mg chemical/kg body weight/day (Table 1-2)
RfD_i	Inhalation Reference Dose	mg chemical/kg body weight/day (Table 1-2)
CSF_i	Cancer slope factor, inhalation	$(mg/kg/day)^{-1}$ (Table 1-2)
CSF_o	Cancer slope factor, oral	$(mg/kg/day)^{-1}$ (Table 1-2)
BW_a	Body weight, adult	70 kg
BW_c	Body weight, child	15 kg
AT_n	Averaging time for noncancer effects	ED x 365 days
AT_c	Averaging time for cancer effects	70 yr x 365 days/yr
IRA_a	Inhalation rate, adult	20 m^3/day

IRA_c	Inhalation rate, child	10 m^3/day
InF_{adj}	Inhalation factor, age-adjusted	11 (m^3·yr/kg·days)
IFS_{adj}	Soil ingestion factor, age-adjusted	114 mg·yr/kg·day
SFS_{adj}	Skin contact factor, age-adjusted	504 mg·yr/kg·days
IRS_c	Soil ingestion rate, child	200 mg/day
IRS_a	Soil ingestion rate, adult	100 mg/day
IRS_i	Soil ingestion rate, industrial	50 mg/day
SA_a	Exposed body surface area, adult	5700 cm^2
SA_c	Exposed body surface area, child	2900 cm^2
VF_s	Volatilization factor for soil	chemical specific (Table 2-3)
PEF	Particulate emission factor	1.32 x 10^9 m^3/kg
ABS	Dermal absorption factor, chemical specific (see Table 2-4)	12 hr cumulative, residential 8 hr cumulative, industrial
AF_a	Soil-to-skin adherence factor, adult	0.08 mg/cm^2
AF_c	Soil-to-skin adherence factor, child	0.3 mg/cm^2
ED_{tot}	Exposure duration, total	30 yr
ED_r	Exposure duration, residential	30 yr
ED_c	Exposure duration, child	6 yr
ED_i	Exposure duration, industrial	25 yr
EF_r	Exposure frequency, residential	350 days/yr
EF_i	Exposure frequency, industrial	250 days/yr

SOURCE: Derived from USEPA 1996b, with modifications

3.3 SOIL SCREENING LEVELS (SSLs)

Soil screening levels are derived only for residential exposure scenarios (USEPA, 1996c). SSLs for surface soils include separate calculations for direct ingestion of soil particles and inhalation of fugitive dust particles. Exposure through dermal contact with contaminated surface soils is also considered a possible exposure pathway; however, incorporation of the dermal pathway is considered to be limited by the available quantitative data on dermal absorption rates for specific chemicals. USEPA (1996c) notes that if the estimated dermal absorption of a chemical is greater than 10%, as in the case of pentachlorophenol, the ingestion SSL should be divided in half to account for the assumption that exposure via the dermal route is equivalent to the ingestion route.

SSLs for subsurface soils address two exposure pathways: ingestion of ground water contaminated as a result of the migration of the chemicals through the soil to the underlying aquifer, and inhalation of volatile compounds released from soil. Groundwater is not considered a probable concern at most sites (see discussion in Section 1.3.3 and Appendix E). Site specific information is necessary to assess screening levels based on concerns about the potential of agent being a source of risk from groundwater contamination. Therefore this pathway is not included in the following calculations. The parameters used in the SSL equations are listed in Table 3-3. The abbreviations of the parameters (without the subscripts) are those used by OSWER (USEPA, 1996c).

The overall SSL methodology involves assessing each pathway separately and selecting the most conservative value (most sensitive exposure pathway) as a screening level. The pathway however should be consistent with realistic site conditions (i.e. the pathway should be considered a completed pathway of exposure).

3.3.1 SSL for Ingestion of Contaminants in Residential Soil - Noncancer Endpoint. The equation for deriving an SSL based on noncancer effects for ingestion of contaminated residential soil is as follows (USEPA, 1996c):

$$SSL = \frac{THQ \times BW_c \times AT_n \times 365\ days/yr}{1/RfD_o \times 10^{-6}\ kg/mg \times EF_r \times ED_c \times IR_c} \quad (3\text{-}9)$$

3.3.2 SSL for Ingestion of Contaminants in Residential Soil - Cancer Endpoint. The equation for deriving an SSL based on cancer effects for ingestion of contaminated residential soil is as follows (USEPA, 1996c):

$$SSL = \frac{TR \times AT_c \times 365\ days/yr}{SF_o \times 10^{-6}\ kg/mg \times EF_r \times IF_{soil/adj}} \quad (3\text{-}10)$$

3.3.3 SSL for Inhalation of Fugitive Dust in Residential Soil - Noncancer Endpoint. The equation for deriving an SSL based on noncancer effects for inhalation of fugitive dusts from residential surface soil is as follows (USEPA, 1996c):

$$SSL = \frac{THQ \times AT_n \times 365\ days/yr}{EF_r \times ED_r \times (\frac{1}{RfC} \times \frac{1}{PEF})} \quad (3\text{-}11)$$

3.3.4 SSL for Inhalation of Fugitive Dust in Residential Soil - Cancer Endpoint. The equation for deriving an SSL based on cancer effects for inhalation of fugitive dusts from residential surface soil is as follows (USEPA, 1996c):

$$SSL = \frac{TR \times AT_c \times 365\ days/yr}{URF \times 1{,}000\ \mu g/mg \times EF_r \times ED_r \times (\frac{1}{PEF})} \quad (3\text{-}12)$$

3.3.5 SSL for Inhalation of Volatile Organics in Residential Soil - Noncancer Endpoint. The equation for deriving an SSL based on noncancer effects for inhalation of volatile organics released from residential subsurface soil is as follows (USEPA, 1996c):

$$SSL_v = \frac{THQ \times AT_n \times 365\ days/yr}{EF_r \times ED_r \times (\frac{1}{RfC} \times \frac{1}{VF})} \quad (3\text{-}13)$$

The volatilization factor (VF) is derived from Equation A-24 in Appendix A. Because the equation to calculate an SSL for inhalation of volatiles from contaminated soils assumes an infinite source, it can violate mass-balance considerations, especially for small sources. The Soil Screening Guidance, therefore, also includes a method for calculating mass-limit SSLs when the size (i.e., area and depth) of the contaminated soil source is known or can be estimated with confidence. The mass-limit VF is derived from the following equation (USEPA, 1996c):

$$VF = Q/C \times \frac{[T \times (3.15 \times 10^7\ s/yr)]}{(\rho_b \times d_s \times 10^6\ g/Mg)} \quad (3\text{-}14)$$

where:

VF	=	Volatilization factor
Q/C	=	Inverse of mean concentration at center of a square source (USEPA default = 68.81 g/m^2-s per kg/m^3)
T	=	Exposure interval (USEPA default = 9.5×10^8 s)
ρ_b	=	Dry soil bulk density (USEPA default = 1.5 kg/L or Mg/m^3)
d_s	=	Average source depth in m (site-specific)

3.3.6 SSL for Inhalation of Volatile Organics in Residential Soil - Cancer Endpoint. The equation for deriving an SSL based on cancer effects for inhalation of volatile organics released from residential subsurface soil is as follows (USEPA, 1996c):

$$SSL_v = \frac{TR \times AT_a \times 365\ days/yr}{URF \times 1{,}000\ \mu g/mg \times EF_r \times ED_r \times (\frac{1}{VF})} \quad (3\text{-}15)$$

The VF is derived from Equation 2-1. Because the equation to calculate a SSL for inhalation of volatiles from contaminated soils assumes an infinite source, it can violate mass-balance considerations, especially for small sources. The Soil Screening Guidance, therefore, also includes a method for calculating mass-limit SSLs when the size (i.e., area and depth) of the contaminated soil source is known or can be estimated with confidence (see Section 3.3.5).

3.3.7 SSL for Migration of Contaminants to Ground Water

As stated by USEPA (1996c), the simplifying assumptions used in deriving SSLs based on migration of contaminants to ground water include the following:

a. Infinite source (steady-state concentrations maintained over the exposure period).
b. Uniformly distributed contamination from the surface to the top of the aquifer.
c. No contaminant attenuation (i.e., adsorption, biodegradation, chemical degradation) in soil.
d. Instantaneous and linear equilibrium soil/water partitioning.
e. Unconfined, unconsolidated aquifer with homogeneous and isotropic hydrologic properties.
f. Receptor well at the downgradient edge of the source and screened within plume.
g. No contaminant attenuation in the aquifer.
h. Contaminant not present as nonaqueous phase liquid (NAPL). If NAPL is present, then the SSL does not apply.

The equation used to derive an SSL based on migration of the chemical contaminant to ground water is as follows (USEPA, 1996c):

$$SSL = C_w \left[K_d + \frac{(\Theta_w + \Theta_a H')}{\rho_b}\right] \quad (3\text{-}16)$$

where:

C_w = Target soil leachate concentration; nonzero MCLG, MCL, or HBL x DAF (in mg/L)
K_d = Soil-water partition coefficient in L/kg (chemical-specific = K_{oc} x f_{oc})
K_{oc} = Soil organic carbon-water partition coefficient in L/kg (chemical -specific)
f_{oc} = Fraction organic carbon in soil (0.002)
Θ_w = Water-filled soil porosity (0.3 L_{water}/L_{soil})
Θ_a = Air-filled soil porosity (n - Θ_w)
n = Soil porosity in Lpore/Lsoil [1-(ρ_b/ρ_s)]
ρ_b = Dry soil bulk density (1.5 kg/L)
ρ_s = Soil particle density (2.65 kg/L)
H′ = Dimensionless Henry's Law Constant (chemical-specific)

The use of the above equation to calculate an SSL assumes an infinite source of contaminants extending to the top of the aquifer. Contaminants at sites with shallow sources, thick unsaturated zones, degradable contaminants, or unsaturated zone characteristics (e.g., clay layers) may attenuate before they reach ground water. In such cases unsaturated zone models and a mass-limit SSL should be calculated when the area and depth (i.e., volume) of the source are known or can be estimated reliably (see Section 3.3.7.3) (USEPA, 1996d).

3.3.7.1 Health-Based Limits (HBLs)

If a drinking water standard (e.g. Maximum Contaminant Level) is not available to determine the target soil leachate concentration, the C_w can be derived from an HBL which is the oral RfD for the chemical multiplied by the average body weight of 70 kg and divided by the daily water consumption rate of 2 L. Thus, the HBL for a chemical with an oral RfD of 1 mg/kg/day would be 35 mg/L, and the target soil leachate concentration would be 700 mg/L (using a 20-fold dilution factor). For a carcinogen, the HBL can be fixed at the drinking water concentration corresponding to a specific risk level.

3.3.7.2 Derivation of the Dilution Factor

As soil leachate moves through the soil and ground water, contaminant concentrations are attenuated by adsorption and degradation (USEPA, 1996c). In the aquifer, dilution by ground water further reduces contaminant concentrations. This reduction in concentration can be expressed by a dilution attenuation factor (DAF), defined as the ratio of soil leachate concentration to receptor point concentration. USEPA's Soil Screening Guidance addresses only one attenuation process -- contaminant dilution in ground water. Furthermore, because of the uncertainty resulting from the wide variability in

subsurface conditions, a default DAF of 20 has been selected as protective for contaminated soil sources up to 0.5 acres in size. Thus, if the health-based limit for ground water is 1 mg/L, then the target soil leachate concentration is 20 mg/L. A DAF of 20 has been used in the calculations of the SSLs for the chemical warfare agents. USEPA notes that because SSLs based on migration to ground water are very sensitive to DAF, site-specific dilution factors should be calculated whenever possible.

3.3.7.3 Mass-Limit SSL for Migration to Ground Water

Because the SSL for ground water assumes an infinite source, it can violate mass-balance considerations, especially for small sources. The Soil Screening Guidance, therefore, also includes a method for calculating mass-limit SSLs when the size (i.e., area and depth) of the contaminated soil source is known or can be estimated with confidence. The mass-limit SSL can be estimated using the following equation (USEPA, 1996c):

$$SSL_{gw} = \frac{(C_w \; x \; I \; x \; ED)}{\rho_b \; x \; d_s} \qquad (3\text{-}17)$$

where:
SSL = Soil Screening Level (mg/kg)
CW = Target soil leachate concentration in mg/L (nonzero MCLG, MCL, or HBL x dilution factor)
I = Infiltration rate (0.18 m/yr)
ED = Exposure duration (70 yr)
ρ_b = Dry soil bulk density (1.5 kg/L)
d_s = Depth of source in m (site-specific)

Table 3-3. Parameters used in equations for Soil Screening Levels (SSLs)

Abbrev.	Definition	Value
SSL	Soil Screening Level	mg chemical/kg soil
THQ	Toxicity Hazard Quotient	1
TR	Target Cancer Risk	10^{-5}, residential
RfD_o	Oral Reference Dose	mg/kg/day (Table 1-2)
RfC	Inhalation Reference Concentration	mg/m^3 (Table 1-2)
URF	Inhalation unit risk factor	$(\mu g/m^3)^{-1}$
CPS_o	Cancer slope factor, oral	$(mg/kg/day)^{-1}$ (Table 1-2)

BW_c	Body weight, child	15 kg
AT_n	Averaging time for noncancer effects	6 yr, child 30 yr, adult
AT_c	Averaging time for cancer effects	70 yr
IR_c	Soil ingestion rate, child	200 mg/day
$IF_{soil/adj}$	Soil ingestion rate, age-adjusted	114 mg·yr/kg·day
ED_r	Exposure duration, residential	30 yr
ED_c	Exposure duration, child	6 yr
EF_r	Exposure frequency, residential	350 days/yr
PEF	Particulate Emission Factor	1.32 x 109 m^3/kg

SOURCE: Derived from USEPA 1996c, with modifications

4. AGENT HD

HBESLs for agent HD, as derived from the algorithms presented in Section 3, are summarized in Table 4-1. The toxicity values and chemical-specific parameter values used to calculate the HBESLs are listed in Table 4-2. As HD is a known carcinogen, both cancer and noncancer endpoints are evaluated.

For noncancer endpoints an oral RfD of 0.000007 mg/kg/day is used. The inhalation RfD is derived from the DHHS/Army air control limit of 0.0001 mg/m^3 by assuming an inhalation rate of 20 m^3/day and a body weight of 70 kg. The resulting inhalation RfD is 0.00003 mg/kg/day. The exposure parameters used to calculate the RBCs, PRGs and SSLs are described in detail in Sections 2 and 3.

Table 4-1. Summary of calculated HBESLs for agent HD

Method (units)	Media, Scenario (pathways)	Noncancer Derived Value	Cancer[a] Derived Value	HBESL
Region III				
RBC (mg/kg)	Soil, residential (ingestion)	0.55	0.83[b]	0.55
RBC (mg/kg)	Soil, commercial/industrial (ingestion)	14	74[c]	14
Region IX				
PRG (mg/kg)	Soil, residential (ingestion, vapor inhalation, dermal)	0.4	0.01[b]	0.01[b]
PRG (mg/kg)	Soil, commercial/industrial (ingestion, vapor inhalation, dermal)	4.5	0.3[c]	0.3[c]
OSWER				
SSL (mg/kg)	Soil, residential (ingestion)	0.55	0.83[b]	
SSL (mg/kg)	Soil, residential (inhalation of dusts)	1.4×10^5	378[b]	
SSL (mg/kg)	Soil, residential (inhalation of volatiles)	5.9	0.016[b]	0.016[b]
SSL (mg/kg)	Soil, residential (migration to ground water)	site-specific[d]	site-specific[d]	

[a] Oral slope factor of 7.7 (mg/kg/day)$^{-1}$ (see Section 1.2.4)

[b] Target cancer risk level of 10^{-5}

[c] Target cancer risk level of 10^{-4}

[d] Because the potential for migration to ground water is quite low, it is recommended that a site-specific analysis of this HBESL be conducted only for those situations where ground-water contamination water is a concern

Table 4-2. Toxicity values and environmental parameters for agent HD

Parameter	Value	Units
Oral Reference Dose	0.000007	mg/kg/day
Air exposure limit	0.0001	mg/m^3
Inhalation Reference Dose	0.00003	mg/kg/day
Oral slope factor	7.7	$(mg/kg/day)^{-1}$
Inhalation unit risk	0.085	$(\mu g/m^3)^{-1}$
Inhalation slope factor	300	$(mg/kg/day)^{-1}$
Dermal absorption factor[d]	5.6/12 hr (residential) 8.4/8 hr (industrial)	percent, from soil
Vapor pressure[a]	0.11	mm Hg at 25°C
Solubility[a]	0.92	g/L at 22°C
Henry's Law Constant (H)[b]	2.1×10^{-5}	$atm \cdot m^3/mol$
Volatilization factor (VF_s)[b]	5.62×10^4	m^3/kg
Soil-water partition coefficient (K_d)[c]	0.266	unitless
Hydrolysis half-life[e]	0.083	hr at 22°C (acidic)
Persistence in soil	0.038[e] - <1.0[a] 1+[a] - 3[e]	yr, on soil surface yr, buried in soil

[a] Value from Rosenblatt et al., 1995
[b] see Appendix A
[c] $K_d = K_{oc} \times f_{oc}$; f_{oc} = 0.006 g organic carbon/g soil (OSWER default); K_{oc} = soil organic carbon-water partition coefficient ($\log K_{oc} = 1.377 + 0.544 \log K_{ow}$; where K_{ow} = water-octanol partition coefficient)
[d] See Section 2.3.2.2 and Appendix H
[e] Value from DA, 1974

The derivation of cancer-based HBESLs for agent HD is complicated by several uncertainties associated with the quantification of the carcinogenic potency of the agent (see discussion in Section 1.2.4). Oral slope factors ranging from 1.6 to 95 $(mg/kg/day)^{-1}$ have been derived for HD. In developing HBESLs in this report, the geometric mean value of 7.7 $(mg/kg/day)^{-1}$ is used. An inhalation slope factor of 300 $(mg/kg/day)^{-1}$ was estimated from the inhalation unit risk recommended by USEPA (1991b) and identified as an interim value by OTSG (DA, 1996a). The target cancer risk level is a risk management

decision that should be made on a site-specific basis. However, a single value is needed to calculate predetermined HBESLs. In this document, a target cancer risk level of 10^{-5} is used to calculate residential HBESLs and a target cancer risk level of 10^{-4} is used to calculate industrial/commercial HBESLs. The rationale for using these risk levels is discussed in Section 1.3.2.

4.1 RISK-BASED CONCENTRATIONS (RBCs)

The soil RBCs for HD are based on a single exposure pathway, incidental ingestion of contaminated soil. The maximum RBC is 74 mg/kg soil for commercial/industrial exposure scenario. At this HBESL, the HD dose resulting from the incidental ingestion of 50 mg of soil (the USEPA default for soil ingestion) is approximately 0.003 mg. In comparison, in studies conducted on rats, a dose of 0.03 mg/kg (about 0.01 mg/animal) caused no toxic effects or produced only mild signs of toxicity after repeated exposures for 13 weeks (see Section 1.3.8). This comparison is based on the assumption that the agent is evenly dispersed through the soil; however, it should be emphasized that if the agent is concentrated into discrete masses in the soil, there is a much greater potential for acute toxicity since a dose of only 0.8 mg is known to cause severe damage to the gastric mucosa in experimental animals.

Although RBCs do not directly address dermal exposures, the potential for acute dermal toxicity at the maximum RBC can be estimated. Assuming an exposed skin area of 5700 cm^2 for adults, and a soil-to-skin adherence of 0.08 mg per cm^2 of skin, the amount of soil that may be in contact with the skin is 456 mg and, at the HBESL of 74 mg/kg, this quantity of soil would contain about 0.03 mg of HD (34 µg). If evenly dispersed in the soil, the average amount of HD per square centimeter of exposed skin would be 0.006 µg (34 µg/5700 cm^2). In comparison, amounts as small as 2 µg are likely to cause erythema in many exposed individuals and blistering in some (see Section 1.3.8). As noted above, if the HD is concentrated into discrete masses in the soil, then there is a significantly increased potential for acute toxicity. Obviously, the RBC methodology (which models chronic health risks) would not apply in such cases where acute toxicity is a realistic concern..

4.2 PRELIMINARY REMEDIATION GOALS (PRGs)

The residential and industrial soil PRGs are substantially less than the corresponding soil RBCs; therefore, the potential for acute exposures is considerably reduced.

For PRGs, volatilization of HD is considered a potential exposure pathway; therefore, the VF of 5.62×10^4 m^3/kg is used in the calculations. Because of the relatively large inhalation unit risk, the oral and dermal exposure pathways contribute relatively little to final cancer PRGs. For example, a cancer-based residential soil PRG derived only from the combined oral and dermal pathways is about 0.6 mg/kg, but one based on only the inhalation pathway is 0.01 mg/kg.

The maximum PRGs are 0.4 mg/kg for residential and 4.5 mg/kg for industrial scenarios. At 4.5 mg/kg, the HD air concentration could theoretically equal 0.00008 mg/m³, assuming that the air concentration is a function of the soil concentration (4.5 mg/kg) divided by the VF (5.62 x 10⁶ m³/kg). Rosenblatt et al. (1995) calculated that for an initial HD soil concentration of 1.0 mg/kg (at a depth of 2-3 m and covering 10,000 m²), the theoretical average air exposure concentration downwind (windspeed 10 mph) over 90 days would be 0.0085 µg/m³ (0.0000085 mg/m³). Rosenblatt et al. (1995) noted that empirical evidence and measured reactivity of HD with water suggest that this is a very conservative estimate. In comparison, a CT of 12 mg-min/m³ (0.2 mg/m³ for 60 min) has been reported to be a no-effect level for eye irritation (see Section 1.3.8). The maximum allowable CT for skin effects is 5 mg-min/m³ and for eye effects it is 2 mg-min/m³ (DA, 1974); these values equate to 0.083 and 0.033 mg/m³ for 60-min exposures, respectively.

4.3 SOIL SCREENING LEVELS (SSLs)

The cancer-based SSLs are lower than the noncancer SSLs. For deriving an SSL for inhalation of fugitive dusts in residential soil, the USEPA default PEF of 1.32 x 10⁹ m³/kg is applied. It should be noted that this HBESL is presented here only to show the results of the calculation following USEPA's guidelines, and is by no means a recommendation for use in remediation. USEPA states that the SSL for inhalation of fugitive dust does not need to be routinely calculated for organic compounds because it is usually several orders of magnitude higher than the corresponding generic ingestion SSLs. For derivation of an SSL for inhalation of volatiles released from soils, the VF_s of 5.62 x 10⁴ m³/kg is used. This resulted in a cancer SSL of 0.016 mg/kg, very similar to the residential soil PRG of 0.01 mg/kg, indicating again that the inhalation pathway is a primary factor for determining the soil screening level.

An SSL for migration to ground water was not calculated for agent HD. The methodology for this SSL assumes an infinite source and no degradation, conditions which are not likely to apply to HD. The actual potential for agent HD migration to ground water is considered to be quite low (see Appendix E). For this reason, it is recommended that a site-specific analysis be conducted for those situations where ground-water contamination is a concern.

Although HD may remain in the soil for months to years, this material is usually present in the form of encapsulated globules, the coating of which prevents further dissolution and degradation (Rosenblatt et al., 1995). In such cases if the capsules are broken, the potential for an acute hazard is high. HBESLs should not be applied to such situations, but rather only to the residual contamination following removal and disposal of the larger masses of agent.

4.4 SUMMARY

Because it incorporates multipathway exposures, the PRG methodology yields the most conservative HBESLs, and for the selected target cancer levels, the cancer-based PRG model yields levels that are more conservative than the noncancer PRGs. However, as noted in Section 1.3.7, when toxic effects of a chemical are not expected to be additive across pathways, PRGs may be overly conservative. To some degree, this may be the case for vesicants such as HD. Oral exposures to HD are likely to affect primarily the lining of the gastro-intestinal tract; dermal exposures target the skin; and inhalation exposures may damage the respiratory tract (and possibly also affect the eyes and skin). RBCs for HD may therefore be adequately protective. However, site-specific evaluation of potential inhalation and dermal pathways (including potential for acute effect levels) may need to be evaluated. SSLs are very similar to the residential PRGs, due to the impacts of including the inhalation pathway.

5. AGENT VX

The HBESLs for VX, as derived from the algorithms presented in Section 3, are summarized in Table 5-1. The toxicity values and the environmental parameter values used to calculate the HBESLs are listed in Table 5-2. The exposure parameters used to calculate the RBCs, PRGs, and SSLs are described in detail in Sections 2 and 3. The oral RfD for VX is 6×10^{-9} mg/kg/day. The estimated inhalation RfD for VX of 9×10^{-8} mg/kg/day was derived from recent suggested revisions to the DHHS/Army control limit (currently 0.000003 mg/m^3, suggested modification is an order of magnitude lower at 0.0000003 mg/m^3) by assuming an inhalation rate of 20 m^3/day and a default body weight of 70 kg. Because there is no evidence that VX is carcinogenic, HBESLs were calculated only for noncarcinogenic effects.

Table 5-1. Summary of calculated HBESLs for agent VX

Method (units)	Media, Scenario (pathways)	Derived Value	HBESL Noncancer Only
Region III			
RBC (mg/kg)	Soil, residential (ingestion)		0.047
RBC (mg/kg)	Soil, commercial/industrial (ingestion)		1.2
Region IX			
PRG (mg/kg)	Soil, residential (ingestion, dust inhalation, and dermal)		0.042
PRG (mg/kg)	Soil, commercial/industrial (ingestion, dust inhalation, and dermal)		1.1
OSWER			
SSL (mg/kg)	Soil, residential (ingestion)	0.047	0.047
SSL (mg/kg)	Soil, residential (inhalation of dusts)	410	
SSL (mg/kg)	Soil, residential (inhalation of vapors)	0.3	
SSL (mg/kg)	Soil, residential (migration to ground water)	site-specific[a]	

[a] Because the potential for migration to ground water is quite low, it is recommended that a site-specific analysis of this SSL be conducted only for those situations where ground-water contamination is a concern.

Table 5-2. Toxicity values and environmental parameters for agent VX

Parameter	Value	Units
Oral Reference Dose	0.0000006	mg/kg/day
Inhalation Exposure Limit	0.000003	mg/m^3
Inhalation Reference Dose	0.00000009	mg/kg/day
Dermal absorption factor	0.27[f]	percent per hr from soil
Vapor pressure[a]	0.0007	mm Hg
Water solubility[a]	10-50[h]	g/L
Henry's Law Constant (H)[b]	3.5×10^{-9}	$atm \cdot m^3/mol$
Volatilization factor (VF_s)[c]	9.67×10^5	m^3/kg
Soil-water partition coefficient (K_d)[d]	1.962	NA
Hydrolysis half-life[a]	50 (pH 9) - 2000 (pH 5)	hr
Persistence in soil	2-6[g] <90[e]	days

[a] Value from MacNaughton and Brewer, 1994
[b] Value from Small, 1984
[c] see Appendix A
[d] $K_d = K_{oc} \times f_{oc}$; f_{oc} = 0.006 g organic carbon/g soil (OSWER default); K_{oc} = soil organic carbon-water partition coefficient ($\log K_{oc} = 1.377 + 0.544 \log K_{ow}$; where K_{ow} = water-octanol partition coefficient)
[e] Value from Rosenblatt et al., 1995, for worst-plausible conditions
[f] see Section 2.3.2.2 and Appendix H
[g] Value from DA, 1974
[h] Value of 30g/L used in calculations

5.1 RISK-BASED CONCENTRATIONS (RBCs)

The equations for calculating USEPA Region III RBCs (USEPA, 1996a) are given in Section 3.1. The soil RBC is based solely on incidental ingestion of contaminated soil. The industrial soil RBC is 1.2 mg/kg, and the dose resulting from the incidental ingestion of 50 mg of soil would be approximately 0.00006 mg VX. In tests on humans, an oral dose of about 0.1 mg (calculated from a reported dose of 0.0014 mg/kg/day and a default body weight of 70 kg) caused no signs of toxicity even after 7 days of exposure (see Section 1.3.8).

5.2 PRELIMINARY REMEDIATION GOALS (PRGs).

The USEPA Region IX equations for PRGs are given in Section 3.2. The dermal absorption factor used in the calculation of the residential soil PRGs is 3.24% for a 12-hour period. The dermal absorption value used for the industrial soil PRG is 2.2% for an 8-hour period. The inhalation pathway is not included in the soil PRG because VX is not expected to volatilize from soil (Henry's Law Constant less than 1×10^{-5} atm-m^3/mol). Instead, the VF_s in the soil PRG equations is replaced with the particulate emission factor (PEF = 1.32×10^9 m^3/kg) to account for exposure through fugitive dust emissions. Assuming an exposed skin area of 5700 cm^2 for adults, and a soil-to-skin adherence of 0.08 mg per cm^2 of skin, the amount of soil that may be in contact with the skin is 456 mg and, at the HBESL of 1.1 mg/kg, this quantity of soil would contain about 0.5 µg of VX. In comparison, mild signs of toxicity were reported in individuals receiving a percutaneous dose of 320 µg (see Section 1.3.8).

5.3 SOIL SCREENING LEVELS (SSLs)

The equations for calculating USEPA OSWER SSLs (USEPA, 1996a) are given in Section 3.3. The residential soil SSL is identical to the residential soil RBC. For deriving an SSL for inhalation of fugitive dusts in a residential soil, the USEPA default PEF of 1.32×10^9 m^3/kg was applied and the resulting SSL is 410 mg/kg. This HBESL is presented here only to show the results of the calculation following USEPA's guidelines, and it is not intended as a recommendation for use in remediation. Other SSLs are more protective and must therefore take precedence. An SSL was also calculated for inhalation of vapors released from soil, even though the likelihood of VX volatilizing from soil is presumed very small. The SSL of 0.3 mg/kg for volatiles is more than 1000-fold more protective than the SSL for dusts; however, the residential soil PRG is still smaller yet. Both the SSL for inhalation pathway and the PRG models are driven by the inhalation pathway, though the SSL approach even more conservatively addresses this pathway by inserting a volatilization factor (VF) in where the PRG assumes only a particulate emission factor (PEF). This difference in the models in some cases (as with the G-agents) results in a lower SSL value than PRG value. But due to the particularly low RfD values for VX (oral and inhalation), the ingestion pathway plays a more significant role, and the additive PRG model, therefore, yields the lowest HBESL value.

An SSL for migration to ground water was not calculated for agent VX. The methodology for this SSL assumes an infinite source and no degradation, conditions which are not likely to apply to VX. The actual potential for agent VX migration to ground water is considered to be quite low (see Appendix E). For this reason, it is recommended that a site-specific analysis be conducted for those situations where contamination of ground water is a concern. The primary hydrolysis product of VX, EA-2192 is expected to be more stable in water, and is considered to be as toxic as VX (see Appendix F). It is recommended that the SSL for migration to groundwater be evaluated for this compound.

5.4 SUMMARY

Because the RfDs (oral and inhalation) of agent VX are particularly low (one to two orders of magnitude lower than the other nerve agents) the impacts of both the oral and inhalation pathways on the end result are significant, whereas with other nerve agents the inhalation pathway has a greater impact on the resulting HBESL value. Though the PRG methodology yields the most conservative HBESLs because they incorporate multipathway exposures, the differences between the PRGs, RBCs, and SSLs are minimal in the case of VX. All methods appear to yield appropriate, valid screening values which represent concentrations that do not present acute or chronic health risks for the given scenarios. Therefore, because the differences between methodologies are relatively insignificant, the PRG method may be used to address concerns regarding additive toxicity across exposure pathways.

6. AGENT GB

The HBESLs for agent GB, as derived from the algorithms given in Section 3, are summarized in Table 6-1. The toxicity values and the environmental parameter values that were used in calculating the HBESLs are listed in Table 6-2. The exposure parameters used to calculate the RBCs, PRGs, and SSLs are described in detail in Sections 2 and 3. The oral RfD for GB is 2×10^{5} mg/kg/day. The estimated inhalation RfD for GB of 9×10^{7} mg/kg/day was derived from the DHHS/Army control limit of 0.000003 mg/m^3 by assuming an inhalation rate of 20 m^3/day and a default body weight of 70 kg. Because there is no evidence that GB is carcinogenic, HBESLs were calculated only for noncarcinogenic effects.

Table 6-1. Summary of calculated HBESLs for agent GB

Type of HBESL	Media, Scenario (pathways)	derived value	HBESL
			Noncancer Only
Region III			
RBC (mg/kg)	Soil, residential (ingestion)		1.6
RBC (mg/kg)	Soil, commercial/industrial (ingestion)		41
Region IX			
PRG (mg/kg)	Soil, residential (ingestion, inhalation, and dermal)		1.3
PRG (mg/kg)	Soil, commercial/industrial (ingestion, inhalation, and dermal)		32
OSWER			
SSL (mg/kg)	Soil, residential (ingestion)	1.6	
SSL (mg/kg)	Soil, residential (inhalation of dusts)	4100	
SSL (mg/kg)	Soil, residential (inhalation of vapors)	0.53	0.53
SSL (mg/kg)	Soil, residential (migration to ground water)	Site-specific*	

* Because the potential for migration to ground water is quite low, it is recommended that a site-specific analysis of this SSL be conducted only for those situations where ground-water contamination is a concern

Table 6-2. Toxicity values and environmental parameters for agent GB

Parameter	Value	Units
Oral Reference Dose	0.00002	mg/kg/day
Inhalation Exposure Limit	0.000003	mg/m^3
Inhalation Reference Dose	0.0000009	mg/kg/day
Dermal absorption factor	0.35[g]	percent per hr from soil
Vapor Pressure[c]	2.94	mm Hg
Solubility[f]	miscible	
Henry's Law Constant (H)[b]	5.34×10^{-7}	$atm \cdot m^3/mol$
Volatilization factor (VF_s)[c]	1.7×10^5	m^3/kg
Soil-water partition coefficient (K_d)[d]	0.208	NA
Hydrolysis half-life[e]	0.5 (pH 9) 250 (pH 6.5 0.5 (pH 5)	hr
Persistence in soil	≤5[a] <30[f]	days

[a] Value from DA, 1974
[b] Value from Small, 1984
[c] see Appendix A
[d] $K_d = K_{oc} \times f_{oc}$; f_{oc} = 0.006 g organic carbon/g soil (USEPA default); K_{oc} = soil organic carbon-water partition coefficient ($\log K_{oc} = 1.377 + 0.544 \log K_{ow}$; where K_{ow} = water-octanol partition coefficient)
[e] Values from MacNaughton and Brewer, 1994
[f] Value from Rosenblatt et al., 1995, for worst-plausible conditions
[g] See Section 2.3.2.2 and Appendix H

6.1 RISK-BASED CONCENTRATIONS (RBCs)

The soil RBC for GB is based solely on ingestion of contaminated soil. The maximum RBC is 41 mg/kg soil for a commercial/industrial scenario. At this HBESL, the dose resulting from ingestion of 50 mg of soil is approximately 0.002 mg GB. In tests on humans, an oral dose of about 0.15 mg (based on a reported dose of 0.002 mg/kg/day and a default body weight of 70 kg) caused mild signs of toxicity (see Section 1.3.8). This dose is about 75 times larger than that calculated from the soil RBC.

6.2 PRELIMINARY REMEDIATION GOALS (PRGs).

The equations for calculating USEPA Region IX PRGs (USEPA, 1996b) are given in Section 3.2. Because GB is not expected to volatilize from soil (Henry's Law Constant = 5.34 x 10^{-7} atm·m^3/mol), the VF_s in the PRG equation is replaced with the particulate emission factor (PEF = 1.32 x 10^9 m^3/kg) to account for exposure through fugitive dust emission. Because the soil PRGs are smaller than the corresponding RBCs, it is not expected that any of the PRGs would pose an acute toxicity hazard by ingestion (see above). The ingestion pathway is a significant driver in the resulting HBESL, though the inhalation pathway is also critical.

The largest PRG for GB is 32 mg/kg soil for a commercial/industrial scenario. At this HBESL and assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5700 cm^2, the total amount of soil on the skin would amount to 456 mg and would contain 0.015 mg of GB. In comparison, experimental studies on humans have shown that 20 mg GB applied to the skin can result in a decrease in blood ChE activity, with no signs or symptoms of toxicity (see Section 1.3.8). A soil PRG of 32 mg/kg soil could theoretically result in a GB air concentration of 0.0002 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (32 mg/kg) divided by the VF (1.7 x 10^5 m^3/kg). In comparison, the estimated no-effect concentration for a 60-min exposure to GB is 0.02 mg/m^3 (see Section 1.3.8).

6.3 SOIL SCREENING LEVELS (SSLs)

The equations for calculating USEPA OSWER SSLs (USEPA, 1996a) are given in Section 3.3. The residential soil SSL is identical to the residential soil RBC. For deriving an SSL for inhalation of fugitive dusts in a residential soil, the USEPA default PEF of 1.32 x 10^9 m^3/kg was applied and the resulting SSL is 4100 mg/kg. This HBESL is presented here only to show the results of the calculation following USEPA's guidelines, and it is not intended as a recommendation for use in remediation. Other SSLs are more protective and must, therefore, take precedence. An SSL was also calculated for inhalation of GB vapors released from soil, in this case using a calculated VF. This SSL is 0.53 mg/kg which is even lower than the PRG value. This is because the SSL model assumes volatility and therefore addresses inhalation of vapors, where the PRG does not (and instead uses a PEF for inhalation of particulate).

An SSL for migration to ground water was not calculated for agent GB. The methodology for this SSL assumes an infinite source and no degradation of agent, conditions which are not likely to apply to GB. The actual potential for agent GB migration to ground water is considered to be quite low (see Appendix E). For this reason, it is recommended that a site-specific analysis be conducted for those situations where ground-water contamination is a concern.

6.4 SUMMARY

In this case the SSL methodology yields the most conservative HBESL, primarily due to the assumption regarding volatility. The SSL does not provide a commercial/industrial value; for this scenario the PRG provides a slightly more conservative value than the RBC because of the additive pathways. Still, differences amongst the HBESLs derived from different models are rather small. Though all methods appear to yield appropriate, valid screening values which represent concentrations that do not present acute or chronic health risks for the given scenarios, the PRG method may be used to address the concern of additive toxicity across exposure pathways, and because the differences between approaches are somewhat minimal. The SSL, though more conservative, may overestimate the impact of the inhalation pathway.

7. AGENT GA

The HBESLs for agent GA, as derived from the algorithms presented in Section 3, are summarized in Table 7-1. The toxicity values and the environmental parameter values used to calculate the HBESLs are listed in Table 7-2. The exposure parameters used to calculate the RBCs, PRGs and SSLs are described in detail in Sections 2 and 3. The oral RfD for GA is 0.00004 mg/kg/day. The estimated inhalation RfD for GA of 9×10^{7} mg/kg/day was derived from the DHHS/Army control limit of 0.000003 mg/m^3 by assuming an inhalation rate of 20 m^3/day and a default body weight of 70 kg. Because there is no evidence that GA is carcinogenic, HBESLs were calculated only for noncarcinogenic effects.

Table 7-1. Summary of calculated HBESLs for agent GA

Method (units)	Media, Scenario (pathways)	Derived Value	HBESL
			Noncancer only
Region III			
RBC (mg/kg)	Soil, residential (ingestion)		3.1
RBC (mg/kg)	Soil, commercial/industrial (ingestion)		82
Region IX			
PRG (mg/kg)	Soil, residential (ingestion, inhalation, and dermal)		2.8
PRG (mg/kg)	Soil, commercial/industrial (ingestion, inhalation, and dermal)		68
OSWER			
SSL (mg/kg)	Soil, residential (ingestion)	3.1	
SSL (mg/kg)	Soil, residential (inhalation of dusts)	4100	
SSL (mg/kg)	Soil, residential (inhalation of vapors)	0.8	0.8
SSL (mg/kg)	Soil, residential (migration to ground water)	site-specific[a]	

[a] Because the potential for migration to ground water is quite low, it is recommended that a site-specific analysis of this SSL be conducted only for those situations where ground-water contamination is a concern.

Table 7-2. Toxicity values and chemical parameters for agent GA		
Parameter	**Value**	***Units***
Oral Reference Dose	0.00004	mg/kg/day
Inhalation Exposure Limit	0.000003	mg/m^3
Inhalation Reference Dose	0.0000009	mg/kg/day
Dermal absorption factor	0.26[e]	percent per hr from soil
Vapor pressure[f]	0.07	mm Hg at 25°C
Water solubility[f]	50-100	g/L
Henry's Law Constant (H)[b]	1.52×10^{-7} [g]	$atm \cdot m^3/mol$
Volatilization factor (VF_s)[c]	2.6×10^5	m^3/kg
Soil-water partition coefficient (K_d)[d]	0.231	
Hydrolysis half-life[a]	8.5	hr. at pH 7, 20°C
Persistence in soil[a]	1-1.5	days

[a] Value from DA, 1974
[b] Estimated from the ratio of the volatility and the solubility (see Appendix A)
[c] See Appendix A for derivation
[d] $K_d = K_{oc} \times f_{oc}$; $f_{oc} = 0.006$ g organic carbon/g soil (USEPA default); K_{oc} = soil organic carbon-water partition coefficient ($\log K_{oc} = 1.377 + 0.544 \log K_{ow}$; where K_{ow} = octanol-water partition coefficient)
[e] See section 2.3.2.2 and Appendix H
[f] Value from MacNaughton and Brewer, 1994
[g] See Section 2.3.2.4

7.1 RISK-BASED CONCENTRATIONS (RBCs)

The equations for calculating USEPA Region III RBCs (USEPA, 1996a) are given in Section 3.1. The soil RBC is based solely on ingestion of contaminated soil. The maximum RBC is 82 mg/kg for the commercial/industrial scenario. At this HBESL, the dose resulting from ingestion of 50 mg of soil is 0.004 mg GA. In comparison, a minimum effect level in humans is estimated to be 0.37 mg (see Section 1.3.8).

7.2 PRELIMINARY REMEDIATION GOALS (PRGs).

The equations for calculating USEPA Region IX PRGs (USEPA, 1996b) are given in Section 3.2. Because of its low Henry's Law Constant, agent GA is not expected to volatilize from soil. For the residential and industrial soil PRGs, the VF_s in the PRG equation is replaced with the particulate emission factor (PEF = 1.32×10^9 m^3/kg) to account for exposure through fugitive dust emission. Because the soil PRGs are equal to or smaller than the corresponding RBCs, it is not expected that any of the PRGs would pose an acute toxicity hazard by ingestion (see above).

The largest PRG for GA is 68 mg/kg soil for a commercial/industrial scenario. At this HBESL and assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5700 cm^2, the total amount of soil on the skin would amount to 456 mg and would contain 0.03 mg of GA. In comparison, it was estimated that the minimum effect level for a percutaneous exposure would be 32-48 mg, and in one experimental human study, a percutaneous dose as high as 400 mg caused no toxic effects but did reduce blood cholinesterase (ChE) activity (see Section 1.3.8). Therefore, the PRG is expected to be protective of any acutely toxic effects under the stated conditions of exposure. A soil PRG of 68 mg/kg soil could theoretically result in a GA air concentration of 0.0003 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (68 mg/kg) divided by the VF (2.6×10^6 m^3/kg). In comparison, a no-effect level of 0.05 mg/m^3 has been estimated by extrapolation from toxicity data for GB (see Section 1.3.8).

7.3 SOIL SCREENING LEVELS (SSLs)

The equations for calculating SSLs (USEPA, 1996c) for GA are given in Section 3.3. The residential soil SSL is identical to the residential soil RBC and is also slightly larger than the residential soil PRG. An SSL for inhalation of fugitive dusts was derived using the USEPA default PEF of 1.32×10^9 m^3/kg, and the DHHS/Army air control limit of 0.3×10^{-6} mg GA/m^3 as an RfC. The resulting SSL is 4100 mg/kg. This HBESL is presented here only to show the results of the calculation following USEPA's guidelines, and it is not intended as a recommendation for use in remediation. Other HBESLs are more protective and must, therefore, take precedence. An SSL was also calculated for inhalation of GA vapors released from soil. This SSL is 0.8 mg/kg which is even lower than the PRG value. This is because the SSL model assumes volatility, and therefore addresses inhalation of vapors, where the PRG does not (and instead uses a PEF for inhalation of particulate).

An SSL for migration to ground water was not calculated for agent GA. The methodology for this SSL assumes an infinite source and no degradation of agent, conditions which are not likely to apply to GA. The actual potential for agent GA migration to ground water is considered to be quite low (see Appendices E and H). For this reason, it is recommended that a site-specific analysis be conducted for those situations where ground-water contamination is a concern.

7.4 SUMMARY

In this case, the SSL methodology yields the most conservative HBESL, primarily due to assumption regarding volatility. The SSL does not provide a commercial/industrial value. For this scenario the PRG provides a slightly more conservative value than the RBC because of the additive pathways. Still, differences amongst the HBESLs derived from different models are rather small. Though all methods appear to yield appropriate, valid screening values which represent concentrations that do not present acute or chronic health risks for the given scenarios, the PRG method may be used to address the concern of additive toxicity across exposure pathways, and because the differences between approaches are somewhat minimal. The SSL, though more conservative, may overestimate the impact of the inhalation pathway.

8. AGENT GD

The HBESLs for agent GD, as derived from the algorithms given in Section 3, are summarized in Table 8-1. The toxicity values and the environmental parameter values that were used to calculate the HBESLs are listed in Table 8-2. The exposure parameters used to calculate the RBCs, PRGs and SSLs are described in detail in Sections 2 and 3. The oral RfD for agent GD is 0.000004 mg/kg/day. The estimated inhalation RfD for GD of 3×10^{-7} mg/kg/day was derived from the DHHS/Army control limit of 0.000001 mg/m^3 by assuming an inhalation rate of 20 m^3/day and a default body weight of 70 kg. Because there is no evidence that agent GD is carcinogenic, HBESLs were calculated only for noncarcinogenic effects.

Table 8-1. Summary of calculated HBESLs for agent GD

Method (units)	Media, Scenario (pathways)	Derived Value	HBESL
			Noncancer Only
Region III			
RBC (mg/kg)	Soil, residential (ingestion)		0.31
RBC (mg/kg)	Soil, commercial/industrial (ingestion)		8.2
Region IX			
PRG (mg/kg)	Soil, residential (ingestion, dust inhalation, and dermal)		0.22
PRG (mg/kg)	Soil, commercial/industrial (ingestion, dust inhalation, and dermal)		5.2
OSWER			
SSL (mg/kg)	Soil, residential (ingestion)	0.31	
SSL (mg/kg)	Soil, residential (inhalation of dusts)	4100	
SSL (mg/kg)	Soil, residential (inhalation of vapors)	0.18	0.18
SSL (mg/kg)	Soil, residential (migration to ground water)	site-specific[a]	

[a] Because the potential for migration to ground water is quite low, it is recommended that a site-specific analysis of this SSL be conducted only for those situations where ground-water contamination is a concern.

Table 8-2. Toxicity values and environmental parameters for agent GD

Parameter	Value	Units
Oral Reference Dose	0.000004	mg/kg/day
Inhalation Exposure Limit	0.000003	mg/m^3
Inhalation Reference Dose	0.0000003	mg/kg/day
Dermal absorption factor	0.78[d]	percent per hr from soil
Vapor pressure[a]	0.40	mm Hg
Water solubility[a]	20-30	g/L
Henry's Law Constant (H)[b]	4.56×10^{-6}	$atm \cdot m^3/mol$
Volatilization factor (VF_s)[b]	1.7×10^5	m^3/kg
Soil-water partition coefficient (K_d)[c]	1.404	NA
Hydrolysis half-life[e]	45	hr at pH 6.65, 25°C
Persistence in soil	ND	

[a] Value from MacNaughton and Brewer, 1994
[b] See Appendix A
[c] $K_d = K_{oc} \times f_{oc}$; f_{oc} = 0.006 g organic carbon/g soil (USEPA default); K_{oc} = soil organic carbon-water partition coefficient ($\log K_{oc} = 1.377 + 0.544 \log K_{ow}$; where K_{ow} = octanol-water partition coefficient)
[d] See section 2.3.2.2 and Appendix H
[e] Value from DA, 1974

8.1 RISK-BASED CONCENTRATIONS (RBCs)

The equations for calculating USEPA Region III RBCs (USEPA, 1996a) are given in Section 3.1. The soil RBC is based solely on ingestion of contaminated soil. The maximum RBC is 8.2 mg/kg for a commercial/industrial scenario. At this HBESL, the dose resulting from ingestion of 50 mg of soil is 0.0004 mg GD. In comparison, a minimum effect level in humans is estimated to be 0.09 mg for oral exposures (see Section 1.3.8).

8.2 PRELIMINARY REMEDIATION GOALS (PRGs)

The equations for calculating USEPA Region IX PRGs (USEPA, 1996b) are given in Section 3.2. Because of its low Henry's Law Constant, agent GD is not expected to volatilize from soil. Therefore, the VF_s in the PRG equation is replaced with the particulate emission factor (PEF = 1.32 x 10^9 m^3/kg) to account for exposure through fugitive dust emission. Because the soil PRGs are equal to or smaller than the corresponding RBCs, it is not expected that any of the PRGs would pose an acute toxicity hazard by ingestion (see above).

The largest PRG for GD is 5.2 mg/kg soil for a commercial/industrial scenario. At this HBESL and assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5700 cm^2, the total amount of soil on the skin would be 456 mg and would contain 0.002 mg of GD. In comparison, it has been estimated that the minimum effect levels for percutaneous exposures is 11 mg (see Section 1.3.8).

A soil PRG of 5.2 mg/kg soil could theoretically result in a GD air concentration of 0.00005 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (5.2 mg/kg) divided by the VF (1.7 x 10^9 m^3/kg). In comparison, a no-effect level of 0.013 mg/m^3 has been estimated by extrapolation from toxicity data for GB (see Section 1.3.8).

8.3 SOIL SCREENING LEVELS (SSLs)

The equations for calculating SSLs (USEPA, 1996c) for GD are given in Section 3.3. An SSL for inhalation of fugitive dusts was derived using the USEPA default PEF of 1.32 x 10^9 m^3/kg, and the DHHS/Army air control limit of 0.3 x 10^{-6} mg/m^3 as an RfC. The SSL for inhalation of GD vapors, as derived using the VF of 1.7 x 10^5 m^3/kg, is 0.18 mg/kg. This SSL value is even lower than the PRG value. This is because the SSL model assumes volatility, and therefore addresses inhalation of vapors, where the PRG does not (and instead uses a PEF for inhalation of particulates).

An SSL for migration to ground water was not calculated for agent GD. The methodology for this SSL assumes an infinite source and no degradation of agent, conditions which are not likely to apply to GD. The actual potential for agent GD migration to ground water is considered to be quite low (see Appendix E). For this reason, it is recommended that a site-specific analysis be conducted for those situations where ground-water contamination is a concern.

8.4 SUMMARY

In this case the SSL methodology yields the most conservative HBESL, primarily due to assumption regarding the volatility. The SSL does not provide a commercial/industrial value; for this scenario the PRG provides a slightly more conservative value than the RBC because of the additive pathways. Still, differences among the HBESLs derived from different models are rather small. Though all methods appear to yield appropriate, valid screening values which represent concentrations that do not present acute or chronic health risks for the given scenarios, the PRG method may be used to address the concern of additive toxicity across exposure pathways, and because the differences between approaches are somewhat minimal. The SSL, though more conservative, may overestimate the impact of the inhalation pathway.

9. Lewisite

The HBESLs for Lewisite, as derived from the algorithms given in Section 3, are summarized in Table 9-1. The toxicity values and the environmental parameter values that were used in their derivation are listed in Table 9-2. The exposure parameters used to calculate the RBCs, PRGs and SSLs are described in detail in Sections 2 and 3. The oral RfD for Lewisite is 0.1μg/kg/day. The estimated inhalation RfD of 0.00086 mg/kg/day was derived from the DHHS/Army control limit of 0.003 mg/m^3 by assuming an inhalation rate of 20 m^3/day and a default body weight of 70 kg.

Table 9-1. Summary of calculated HBESLs for Lewisite[a]

Method (units)	Media/Scenario (pathways)	Derived Value	HBESL
			Noncancer Only
Region III			
RBC (mg/kg)	Soil, residential (ingestion)	7.8	7.8
RBC (mg/kg)	Soil, commercial/industrial (ingestion)	200	(7.8)[b]
Region IX			
PRG (mg/kg)	Soil, residential (ingestion, inhalation, and dermal)	0.3	0.3
PRG (mg/kg)	Soil, commercial/industrial (ingestion, inhalation, and dermal)	3.7	3.7
OSWER			
SSL (mg/kg)	Soil, residential (ingestion)	7.8	7.8
SSL (mg/kg)	Soil, residential (inhalation of dusts)	4.1×10^6	
SSL (mg/kg)	Soil, residential (inhalation of vapors)	NA[c]	
SSL (mg/kg)	Soil, residential (migration to ground water)	NA[d]	

[a] Because of rapid hydrolysis, these HBESLs also apply to the degradation product, 2-chlorovinylarsonous acid.
[b] RBC value derived for the commercial/industrial scenario was potentially above acute toxicity levels, therefore the upper bound value of the residential scenario is suggested as a substitute.
[c] SSL cannot be calculated because a Volatilization Factor is not available
[d] SSL cannot be calculated because a K_{ow} is not available

Although Lewisite is a suspect carcinogen because it is an arsenic-based compound (inorganic arsenic has been classified as a known human carcinogen), there are no epidemiological or experimental data verifying its carcinogenicity or quantifying its carcinogenic potency (there are no oral or inhalation

slope factors). Therefore, HBESLs for Lewisite are derived here only for noncarcinogenic endpoints. It is recommended, however, that existing EPA screening levels for inorganic arsenic be used for carcinogenic endpoints.

An experimentally derived skin absorption factor (ABS) is not available for Lewisite; therefore, a default value of 0.1 is used in accordance with USEPA Region IX guidelines for organic compounds (USEPA 1996b). Also, the oral RfD for Lewisite was not applied directly as a dermal RfD, though this procedure is often used by EPA Region IX in absence of a dermal RfD. As described previously, the median threshold dose for blistering has been reported to be 14 µg and a dose as low as 3.5 µg reportedly caused erythema in 27 out of 93 individuals and blisters in 8 of the 93 (see Section 1.3.8). Because the standard methodology (using the oral RfD applied as a dermal RfD) results in a dermal RfD (of 4 µg) which is above a potential dermal effect level, the Lewisite HBESLs were calculated using a dermal RfD based on the existing acute dermal toxicity data which results in an more conservative estimate. Calculations are described in section 9.2 below.

Table 9-2. Toxicity values and environmental parameters for Lewisite

Parameter	Value	Units
Oral Reference Dose	0.0001	mg/kg/day
Inhalation Exposure Limit	0.003	mg/m^3
Inhalation Reference Dose	0.0009	mg/kg/day
Dermal Reference Dose[d]	0.0000017	mg/kg/day
Dermal absorption factor	10	percent
Vapor pressure[a]	0.58	mm Hg
Water Solubility (WS)	0.5[b]	g/L
Henry's Law Constant (H)	NA[b]	$atm \cdot m^3/mol$
Volatilization factor (VF_s)	NA[b]	m^3/kg
Soil-water partition coefficient (K_d)	NA[b]	NA
Hydrolysis half-life	Rapid[c]	
Persistence in soil	"Intermediate"[c]	days

[a] Value from MacNaughton and Brewer, 1994

[b] Because of rapid hydrolysis, estimates of water solubility are not meaningful (Rosenblatt et al., 1975); H, VF and K_d cannot be derived

[c] DA, 1974

[d] Derived from acute toxicity data (see Section 9.2)

9.1 RISK-BASED CONCENTRATIONS (RBCs)

The equations for calculating USEPA Region III RBCs (USEPA, 1996a) are given in Section 3.1. The soil RBC is based solely on ingestion of contaminated soil. The maximum RBC is 200 mg/kg for a commercial/industrial scenario. At this HBESL, the dose resulting from ingestion of 50 mg of soil is 0.01 mg. Experimentally derived minimum effect levels (MELs) in animals range from 0.07 to 2 mg/kg (see Section 1.3.8), equivalent to 0.02 - 0.6 mg per animal. Other data (described below) suggest acute dermal effects at lower dose levels. In all, the HBESL derived for the commercial/industrial scenario appears to be at a level where acute effects could potentially be exhibited under the assumed exposure conditions. Though the limited data do not permit a clear demarcation of what level acute effects would occur, the concern should not be overlooked. For purposes of this document, the HBESL resulting from the RBC *residential* calculation (7.8 mg/kg) is also recommended for application in a commercial/industrial scenario.

At a concentration of 7.8 mg of Lewisite/kg of soil, ingestion of 50 mg of soil yields 0.004 mg Lewisite; a dose which is lower than the estimated MELs.

9.2 PRELIMINARY REMEDIATION GOALS (PRGs)

Because the standard EPA Region methodology in which the oral RfD is applied as a dermal RfD results in a dermal Lewisite RfD of 7 µg, which is above a potential dermal effect level, the Lewisite HBESLs were calculated using a dermal RfD based on the existing acute dermal toxicity data which results in a more conservative estimate. This was accomplished by adjusting the reported effect level of 3.5 µg (see Section 1.2) by a standard factor of 10 to arrive at an estimated no-effect level of 0.35 µg. Because dose-response data are not available to be certain that 0.35 µg is a no-effect level, an additional Modifying Factor of 3 was applied, resulting in a value of 0.12 µg. For a 70 kg person this is equivalent to a dose of 0.0017 µg/kg body weight (0.0000017 mg/kg). This value was then used as the dermal RfD in the PRG equation. The resulting commercial/industrial HBESL calculated for Lewisite is therefore 3.7 mg/kg. Assuming a soil adherence of 0.08 mg per cm^2 of skin (USEPA default) and a total exposed skin area of 5700 cm^2, the total amount of soil on the skin at the HBESL would be 456 mg and would contain 1.7 μg of Lewisite (0.08 mg/cm^2 X 5700 cm^2 = 456 mg x (3.7 mg/kg(/1000000)) = 0.0017 mg = 1.7 μg Lewisite). Under the exposure assumptions used to derive the HBESL of 3.7, the total dose of 1.7 μg would be dispersed over a surface area of 5700 cm^2, resulting in an average exposure per unit of exposed surface area of 0.0003 μg/cm^2 (i.e., 1.7 μg Lewisite / 5700 cm^2). It is assumed that this exposure does not occur at a single point in time but rather over a period of time during the day. Therefore, it is unlikely that acutely toxic effects would occur at this HBESL level of 3.7 mg/kg. *It must be kept in mind that the effect level (3.5 µg) is for pure agent concentrated in a single small area of the skin; whereas, the PRG methodology assumes an even dispersion of the agent throughout the soil. Obviously, the soil PRGs for vesicants such as Lewisite would not apply if the agent is clumped into discrete masses.*

9.3 SOIL SCREENING LEVELS (SSLs)

The equations for calculating USEPA OSWER SSLs (USEPA, 1996a) are given in Section 3.3. An SSL for inhalation of fugitive dusts was derived using the USEPA default PEF of 1.32 x 10^9 m^3/kg, and the DHHS/Army air control limit of 0.003 m/m^3 as an RfC. The resulting SSL is 4.1 x 10^6 mg/kg. This HBESL is presented here only to show the results of the calculation following USEPA's guidelines, and it is not intended as a recommendation for use in remediation. Other HBESLs are more protective and must, therefore, take precedence. A SSL for inhalation of vapors could not be calculated due to data limitation. An SSL for migration to ground water cannot be calculated for Lewisite because of its instability in water. The SSL for the ingestion pathway, 7.8 mg/kg, as always is identical to the residential RBC value. As stated above, this level should be protective against both chronic and acute effects; however, there is uncertainty due to data limitations. Finally, as in the case of the RBCs and PRGs, one should consider CVA (see Appendix F) for screening purposes where Lewisite is a concern.

9.4 SUMMARY

PRGs are the most protective HBESLs for Lewisite , because they incorporate multipathway exposures and specifically allow one to address the dermal pathway and acute toxicity concerns. As noted in Section 1.3.7, PRGs may be overly conservative where toxic effects of a chemical are not expected to be additive across pathways, as is the case of vesicants such as Lewisite, where the primary toxic effect is at the point of contact. However, if acute toxicity is a concern this is irrelevant. In addition, there is evidence that Lewisite may be absorbed systemically even at low doses; therefore, that PRGs may be the most appropriate model to use for this agent. It is also recommended that if rapid degradation of Lewisite is expected, screening levels for the primary degradation product of Lewisite, CVA/Lewisite oxide, be included in the screening process.

10. COMPARISON OF SCREENING METHODS

The screening approaches for soil contamination used by OSWER and USEPA's Regional Offices differ in varying degrees. In all, these approaches encompass single and multiple exposure pathways including ingestion, dermal contact, inhalation of dusts, inhalation of volatiles, and migration to ground water. This section identifies the similarities and differences in these methods by discussing the individual exposure routes, and summarizes their appropriateness for conducting risk assessments for chemical warfare agents.

10.1 Ingestion

USEPA Region III residential soil RBC is identical to the OSWER surface soil screening level in that both are limited to one exposure pathway, that of soil ingestion by children. Either of these HBESLs are appropriate for environmental contaminants that are nonvolatile and have a low potential for dermal absorption. If a contaminant is volatile, it is less likely to pose a significant risk through dermal contact unless its adsorption to soil particles limits volatilization. However, all the agents discussed in this report have relatively low soil adsorption coefficients (see Table 2-3); therefore, binding to soil is not expected to be significant. For the vesicants which have dermal effects, and for agent VX which is considered nonvolatile and is readily absorbed through the skin, any screening levels based on soil ingestion alone should be compared to screening levels based on potential dermal contact with the contaminants.

10.2 Dermal

While USEPA Region III RBCs do not directly address the dermal exposure route, it does (USEPA, 1995a) support the use of the method given in the Superfund Risk Assessment Guidance Document (USEPA, 1989) for estimating dermal exposures. This method can be used to derive a soil screening level specifically for dermal exposures to contaminated soil. Dermal exposures can be estimated from information on the amount of skin surface area exposed, the soil-to-skin adherence factor, and the dermal absorption factor. The estimated absorbed dose is then compared to a dermal RfD to derive the screening level. This approach is equivalent to the dermal exposure *component* of Region IX's soil PRGs for residential and industrial/commercial scenarios. By direct implementation, only the Region IX screening levels directly incorporate this pathway.

Two key factors are used to derive a dermal screening level; the dermal absorption factor and the dermal RfD. The dermal absorption factor is a chemical-specific value which allows for the estimation of the absorbed dose. USEPA Region III has summarized the available pertinent information on dermal absorption values for a range of volatile and semivolatile organic compounds and has recommended a

conservative default value of 10% for semivolatile organic compounds and pesticides (USEPA, 1995a). Similar defaults are used by USEPA Region IX. However, USEPA Region IV recommends 1% as the default for organic compounds (and 0.1% for inorganics) on the basis that skin absorption will be reduced due to binding of the chemicals to the soil. Volatile chemical agents such as the G agents are unlikely to pose a dermal hazard; however, the risks from dermal exposure to VX and HD may be significant. Theoretical estimates of skin absorption of chemical warfare agents in a soil matrix range from 0.27%/hr for VX to 0.70%/hr for HD (Majors, 1997). Based on these estimates, chemical-specific 8-hour cumulative dermal absorption factors were used to calculate industrial soil PRGs and 12-hour cumulative dermal absorption factors were used to calculate soil PRGs for residential and trespasser exposures. These values (see Table 2-4) fall between the 1% default recommended by Region IV and the 10% default recommended by Region IX.

The second key component for deriving a soil screening level for dermal exposures is the dermal RfD. Dermal RfDs for chronic or subchronic exposures are not available for any of the chemical warfare agents. For systemic toxins, a dermal RfD is the equivalent of an absorbed dose RfD and can be estimated from the oral RfD by the use of a chemical-specific gastrointestinal absorption factor. This approach is applicable to the nerve agents which are systemic toxins; however, insufficient data were available to estimate gastrointestinal absorption factors. USEPA Region IX states that, in the absence of chemical-specific gastrointestinal absorption data, the oral RfD can be used in place of the estimated dermal RfD (i.e., a gastrointestinal absorption rate of 100% is assumed). This is the general approach used in this report.

If the effects are localized, and not the result of systemic uptake, as in the case of vesicants, a dermal RfD is more likely to be a function of applied dose rather than the absorbed dose. Thus, for vesicants HD and Lewisite, a dose per unit area of skin may be a more appropriate dermal RfD to compare with the potential skin exposures. Such dermal RfDs are not available for these agents. It should be noted, however, that the critical effect seen in animal toxicity studies on which the oral RfDs for both HD and Lewisite were based, involved pathological changes in the epithelial surface of the gastrointestinal tract, consistent with the vesicant properties of these compounds. For HD, the oral RfD was used instead of a dermal RfD - and the resulting screening levels compared with available data. For Lewisite, comparisons of available acute dermal data suggested that use of the oral RfD was inadequate; therefore a dermal RfD was calculated.

10.3 Migration to Ground Water

The OSWER soil screening level for potential migration of a contaminant to ground water is dependent on a set of simplifying conditions (see Section 3.3.7) including the assumption of an infinite source, uniform distribution in soil, and no attenuation in soil or ground water. It is unlikely that these conditions will be maintained for any of the chemical warfare agents discussed in this report. The agents

are likely to occur only in very limited areas and most are very susceptible to hydrolysis and degradation to less toxic forms. This is particularly true for the nerve agents GA, GB, and GD, whose persistence in soil is usually measured in days (see Section 1.2.3). Agent VX is expected to be more persistent in soils than the G agents because it is relatively nonvolatile and less susceptible to hydrolysis. VX is water soluble (10-50 g/L), and has a relatively low potential for soil adsorption (K_d = 1.962 for soils with organic carbon level of 0.006 g/g: see Table 2-3). Therefore, VX would also be expected to have a greater potential for migration to ground water than the G agents. However, it should be noted that laboratory studies indicate that 90% of VX was degraded after only 2 days when tested in three types of soil [(humic sand, humic loam, and clayey peat (Verweij and Boter, 1976)]. These data indicate that there is little potential for migration to ground water for any of the nerve agents (GA, GB, GD or VX). USEPA notes that for contaminants at sites with shallow sources, thick unsaturated zones, degradable contaminants, or unsaturated zone characteristics (e.g., clay layers), the concentrations of the contaminants may be reduced substantially before they reach the ground water (USEPA, 1996d). In such cases, USEPA recommends the use of unsaturated zone models for soil screening. These models, which are described in more detail in the Technical Background Document (USEPA, 1996d) of the Soil Screening Guidance, may be relevant for environmental screening of the chemical warfare agents. Furthermore, USEPA recommends that mass-limit SSLs be calculated when the area and depth of a contaminated soil source is known, or can be estimated with confidence. The equation for deriving mass-limit SSLs is given in Section 3.3.7.3. Mass-limit SSLs may be more appropriate for the chemical warfare agents than generic ground-water SSLs based on the assumptions mentioned above.

The low potential for the nerve agents to migrate to ground water is supported by the results of the ground-water modeling exercises described in Appendix E. Unlike the SSL approach, these models used information on the rates of agent degradation through hydrolysis.

Agent HD may remain in subsurface soils for years when undisturbed: individual droplets (micelles) of this agent are likely to be encased with a polymeric coating (formed from unhydrolyzed agent and its primary degradation product, thiodiglycol), which prevents further dissolution of the agent into the surrounding soil. In this form, migration of HD to ground water would be unlikely. In addition, any mustard dissolving from such micelles would be subject to rapid hydrolysis since the hydrolysis half-life of dissolved HD agent is less than 10 minutes at environmental temperatures (see Table 1-1). Results of the ground-water modeling exercises described in Appendix E also indicate a very low potential for ground-water contamination by HD.

In the case of Lewisite, this agent is subject to rapid hydrolysis to CVA. Therefore, SSLs for migration to ground water for Lewisite should be based on CVA (see Appendix F).

10.4 Airborne Dust

The OSWER has developed a separate soil screening level for inhalation of contaminated soil particles resuspended in air. This SSL incorporates a default particulate emission factor (PEF, see Section 2.3.3.2) that is dependent on wind speed and vegetative cover. This HBESL results in very high soil values because it assumes that only a small fraction of the contaminated soil will be suspended as dust and inhaled. USEPA states that SSL for inhalation of fugitive dust does not need to be routinely calculated for organic compounds because of the strong likelihood that the ingestion SSL would be more protective. For acutely toxic chemicals such as the warfare agents, the high dust SSL may exceed acutely toxic levels. Therefore, it is unlikely that the SSL for inhalation of dusts will ever be used as an HBESL. Other HBESLs (or PRGs or RBCs) are more conservative and would be used instead. Furthermore, in the case of vesicants, contact of the contaminated dusts with the eyes or skin may pose as great a potential hazard as inhalation of the dusts; therefore, this SSL may greatly underestimate potential risks associated with exposure to nonvolatile vesicant agents.

10.5 Volatiles

The SSL for inhalation of volatile contaminants released from subsurface soils incorporates a chemical-specific VF (see Section 2.3.2.4) that is dependent on the chemical's diffusivity in air and water, its Henry's Law Constant, and its soil adsorption coefficient, as well as several soil characteristics. The VF is derived from a model that calculates the maximum flux of the contaminant from a soil based on soil moisture conditions and on the air-filled soil porosity. It assumes an infinite contaminant source and vapor phase diffusion as the only transport mechanism. Because contaminant sources for chemical warfare agents are likely to be very limited, this SSL may not be applicable to the agents, and the values presented in this report may *over*estimate the potential risks. The OSWER recommends the mass-limit approach when information about the size of the source is known (see Section 3.3.5.1), and it is recommended that this approach be used for chemical warfare agents on a site-specific basis whenever possible.

10.6 Multipathway

USEPA Region IX residential and industrial soil PRGs incorporate three exposure pathways, ingestion of soil, inhalation of volatiles (or particulates) released from soil, and dermal absorption following skin contact (see Sections 3.2.3-3.2.6). For a noncancer endpoint, the residential soil PRG is calculated for a child only. The soil ingestion component of the PRG is identical to residential soil RBC for Region III and the residential soil SSL derived by OSWER. In the inhalation component of the PRG, the Henry's Law Constant (H) of a contaminant is used to determine whether the inhalation pathway is a significant source of exposure, as in the case of the tapwater RBCs and PRGs. Chemicals with an H of 10^{-5} atm-m^3/mol or less and a molecular weight of more than 200 are not considered to pose an inhalation

risk. Based on this definition, HD is the only chemical warfare agent, of those considered in this report, that is expected to be an inhalation hazard from contaminated soils. In most soils, however, hydrolysis (half-life 8.5 minutes) is likely to limit the amount of HD released through volatilization.

If volatilization is considered significant for any soil contaminant, a chemical-specific VF is used in the Region IX soil PRG equation. This VF is derived in an identical manner to that used by OSWER to estimate a VF for use in calculating an SSL for inhalation of volatile organics, and it is subject to the same limitations. A major limitation is the assumption that there is an infinite contaminant source and that vapor phase transport is the only transport mechanism. These assumptions are not likely to apply to the chemical warfare agents which are expected to occur in only limited quantities and may be subject to degradation. Furthermore, the VF is derived from a set of chemical-specific parameters (e.g., air and water diffusivity, Henry's Law Constant, and soil adsorption coefficients). In the case of the chemical warfare agents, most of these parameters were not determined experimentally, but were estimated using predictive models (see Appendix A). Therefore, the derived values and the resultant VFs for the agents, as presented in Table 2-3, have a high level of uncertainty associated with them, and this uncertainty can only be reduced by experimental verification.

If volatilization is not considered significant for any specific contaminant, the Region IX PRG method incorporates a default PEF that accounts for exposures through inhalation of fugitive dusts. This default PEF is identical to that used by OSWER for calculating an SSL for fugitive dusts. Because the PEF is quite large (1.32×10^9 m^3/kg), it has an insignificant effect on the final values when used in the PRG equation. In such cases, the ingestion and dermal pathways are the determining factors.

The dermal portion of the Region IX PRG for residential or industrial soils is identical to the approach used in the Superfund Risk Assessment Guidance for estimating dermal exposures (USEPA, 1989). USEPA Region IX allows for the use of the oral RfD as a surrogate dermal RfD if chemical-specific information on gastrointestinal absorption rates is not available. This is the approach followed in this report.

The use of soil PRGs for HBESLs may be considered most appropriate in those cases where the target organ is the same for each exposure pathway and the effects are expected to be additive. For systemically absorbed compounds, such as the nerve agents VX, GA, GB, and GD, it is usually assumed that the effects are additive across pathways. Therefore, PRGs would be the most appropriate HBESLs. For vesicant agents, different exposure pathways may affect different epithelial tissues and the effects are not likely to be additive. Therefore, for HD and Lewisite, pathway-specific screening levels (RBCs or SSLs) may be more appropriate than some PRGs.

11. SUMMARY AND RECOMMENDATIONS

11.1 GENERAL

Environmental screening levels (referred to by different names by the various USEPA Regions) are low-level concentrations of individual chemicals in environmental media, which, if not exceeded, are unlikely to present a human health hazard for specific exposure scenarios. These 'low-level' concentrations are back-calculated from various USEPA risk assessment models using predetermined, conservative "acceptable risk" quantifiers. These screening levels have been calculated for hundreds of commercial chemicals that are presumed to present potential environmental health impacts at sites where soil has been contaminated. Chemical warfare agents, as chemicals that may be identified as environmental contaminants, may be evaluated with the same health risk assessment methodologies.

During the initial evaluation phase of an environmental health risk assessment, these pre-established environmental screening levels for chemical compounds can aid the assessment process by their use as "action or no-action" determinant criteria. For a specified type of scenario, if the actual soil concentrations were to fall below the established screening level, no further "action" would be deemed necessary. If concentrations were above the screening level, additional "action" would be necessary. This "action" requirement may be met by a variety of procedures to include: performing a detailed site-specific health risk assessment; applying management controls to minimize exposure; implementing treatment/remedial operations; or a combination of these options. By focusing assessment efforts in this manner, screening levels can help to optimize resources and minimize unnecessary expenditures of time and money.

Another benefit of pre-established environmental screening levels is that they allow a means to determine whether analytical detection capabilities for chemical contaminants are adequate. This is particularly beneficial if the compounds are very toxic and the resulting screening levels are extremely low.

These benefits have been demonstrated by the generation and use of screening levels for a wide variety of commercial/industrial contaminants by different USEPA and state regulatory agencies and the responsible regulated communities and industries. The screening approach can reasonably provide similar benefits for those parties involved with determining future action requirements at sites contaminated by unique military compounds such as the chemical warfare agents HD, Lewisite, GA, GB, GD, and VX.

In recommending a set of pre-established HBESLs, however, methodology variations, scientific data limitations and inconsistencies, and risk management issues must be carefully evaluated. Most of these same considerations must be evaluated in detail during site-specific or 'baseline' risk assessments. For screening purposes, some additional degree of 'conservatism' (resulting in media concentrations potentially lower than what might actually pose a significant public health hazard) is necessary than when performing a baseline site-specific risk assessment.

11.2 REVIEW OF SCREENING METHODS

11.2.1 *EPA Region III Risk-Based Concentrations (RBCs)*

RBCs may be acceptable screening levels in those cases where the effects of a compound are not expected to be additive or cumulative across exposure pathways. This may be particularly true for low-level exposures to vesicants if there is no systemic absorption and the critical effect occurs at the point of contact. However, soil RBCs pertain only to the ingestion pathway, and for vesicants or agents that are readily absorbed through the skin, the soil RBCs may underestimate the potential hazard. Dermal exposures should be evaluated when the chemical characteristics or toxicity of a chemical warrant it.

For systemically absorbed contaminants such as the nerve agents, particularly those that exert their toxic effect on the same physiological system regardless of the exposure pathway, RBCs are likely to underestimate the potential hazard.

11.2.2 Region IX Preliminary Remediation Goals (PRGs)

Because soil PRGs incorporate multiple exposure pathways (ingestion, skin contact, and inhalation), they result in lower screening values than the soil RBCs. The appropriateness of the PRGs is contingent on several factors to include: whether all exposure pathways are relevant for a given contaminant, whether the same toxic endpoint occurs regardless of the exposure route, and whether toxicity values (RfDs and/or slope factors) are available for each exposure route or whether they can reasonably be estimated from the ones that are available. In situations where the toxicity endpoints may be different for each exposure pathway, as in the case of the vesicants HD and Lewisite, PRGs may theoretically result in overly conservative HBESLs - however, acute toxicity evaluation should be considered.

The soil PRGs take into account the possibility of inhalation exposures resulting from volatilization of a chemical from subsurface soil (PRGs do not apply to surface spills). According to USEPA Region IX, a chemical's Henry's Law Constant, which is the ratio of its volatility to its water solubility, can be used to determine whether volatilization results in a significant inhalation exposure. As discussed by USEPA (1996d), subsurface volatilization is a function of soil moisture and the partitioning of the chemical between soil pore water and soil pore air (as reflected in a chemical's Henry's Law Constant). Chemicals with a Henry's Law Constant less than 1×10^{-5} atm-m^3/mol and a molecular weight greater than 200 are not expected to volatilize from subsurface soils (USEPA, 1996b), presumably because the chemical will partition primarily to soil pore water.

If USEPA Region IX's approach is followed, none of the nerve agents would be expected to volatilize from subsurface soils because their Henry's Law Constants are below 1×10^{-5} atm-m^3/mol. This conclusion is counterintuitive for a chemical such as agent GB which has a relatively high vapor pressure (2.9 mm Hg at 25 °C). Although this may be partially explained by the fact that GB is totally miscible in

water, there nevertheless remains some degree of uncertainty surrounding the assumption that GB will not volatilize from subsurface soil, particularly from relatively dry soil. For arid conditions, a soil PRG can be calculated for GB using its chemical-specific soil VF. Although the Henry's Law Constant for HD is slightly above 1 x 10^{-5} atm-m^3/mol, its tendency to encapsulate, and quickly hydrolyze when dissolved, is expected to minimize volatilization from subsurface soils. Similarly, Lewisite hydrolyzes rapidly to a nonvolatile product; therefore, volatilization from subsurface soils is not expected to be environmentally relevant.

Where toxicity data exist for specific agents, the predicted levels of exposure at the PRG-derived HBESLs were compared with minimum effect levels for acute toxicity. These calculations indicated that the potential for acutely toxic exposures was low. These estimates were based on certain assumed and plausible conditions of exposure, and do not include all possible exposure situations.

11.2.3 EPA OSWER Soil Screening Levels (SSLs)

The SSL for ingestion of surface soils is derived in a manner identical to that for residential soil RBCs. Both methods are conservatively based on potential exposures to children, considered to be the most susceptible receptor.

The SSLs for inhalation of dusts released from surface soils and for inhalation of volatiles released from subsurface soils, are single pathway screening levels. The SSL for dusts uses a default particulate emission factor that results in extremely high SSL values. As mentioned previously, these SSLs are calculated only to show the results of following USEPA's guidelines; they are not a recommendation for use.

The SSLs for inhalation of volatiles released from subsurface soils is identical to the inhalation component of the soil PRG. It should be noted that this refers to low concentrations of contaminants in subsurface soils, assumes an infinite source of contamination, and requires the calculation of a chemical-specific Volatilization Factor (see Appendix A). When the source is limited, and the size and depth of the contaminated area is known, USEPA recommends deriving a mass-limit SSL with a mass-limit VF (see Section 3.3.5). Mass-limit SSLs are likely to be relevant for chemical agents which are not expected to be widely dispersed and should be calculated whenever site-specific data are available.

The SSLs for migration of contaminants from subsurface soils to ground water requires the use of a set of simplifying assumptions. These assumptions are not likely to apply to the chemical warfare agents because of their expected highly localized distribution in the soil, their relatively rapid degradation, or their expected immobility (HD). Mathematical modeling indicates that the likelihood of any agent migrating to ground water is very low (see Appendix E). For this reason, SSLs for migration to ground water were not calculated for any of the agents. It is recommended that if necessary, ground-water SSLs be evaluated on a site-specific basis.

11.3 CONCLUSIONS

11.3.1 The three EPA methods assessed are very similar; the differences do not generally yield substantially different screening levels. The additive pathway approach incorporated by the PRG Region IX generally results in some of the more conservative (lower) values, primarily due to the additive effects of the inhalation route, and to some degree the dermal route. The SSL inhalation pathway model also produces some of the most conservative values. For the vesicants HD and L, the RBC model must be used cautiously to ensure resulting concentrations do not yield acute effects. In all, the "best" model may be different for different chemicals and situations. The benefits and disadvantages of one method over another are somewhat speculative, but depend on chemical and site/exposure-specific considerations. Ultimately, stakeholders (including site regulators, the public and Army personnel) must evaluate the available information to determine whether the use of a screening approach is warranted and, if so, what models and parameters best suit the situation.

11.3.2 The HBESL values calculated in this document are intended to represent conservative values for use in *screening* contaminated sites for potential human health risks. The degree of 'conservatism' that is truly represented cannot be quantified due to the uncertainties inherent to the risk assessment models. These uncertainties are further compounded by limited data regarding both the chemical warfare agents and the human exposure process. A limitation of the application of the HBESLs for generic scenarios is that, by using a standardized approach and assumptions, unique site-specific variables may be overlooked. Therefore, before application of HBESLs as action/no-action determinants, the user must first evaluate the situation to ensure that certain assumption criteria are met. This includes ensuring that all stakeholders have input to the application of screening levels. However, despite the weaknesses associated with deriving and applying HBESLs, they provide a mechanism to make efficient, consistent, and scientifically based action/no-action decisions when assessing the potential for chronic health effects to exposed populations.

11.3.3 HBESLs are derived on the assumption that exposure will be of chronic duration, which according to USEPA covers a time span of 7 years to a lifetime. However, empirical data and theoretical estimates indicate that soil persistence of the nerve agents is likely to be no more than several months even under the worst-plausible conditions. Current EPA models do not consider environmental degradation; it is therefore quite possible that actual exposure durations/frequencies are significantly overestimated resulting in conservatively "safe" screening levels. This complex issue of degradation should be considered in chemical and site-specific evaluations when using screening levels and may need to be more critically incorporated in a site-specific risk assessment. Depending on many factors - including (but not limited to) environmental conditions and quantities released - persistence of the agent HD in soils could potentially be measured in years (refer to section 1.2.3), mainly as a result of the agent being encapsulated in an inert polymeric coating formed by its hydrolysis products. As noted previously, HBESLs are not applicable to such situations because acutely toxic exposures are possible if such capsules are broken. Soil persistence data for Lewisite are not available; however, the literature indicate that Lewisite would degrade rapidly to CVAA/ Lewisite oxide, which would eventually degrade to inorganic arsenic. CVAA and Lewisite oxide are presumed to be somewhat persistent, however, and as

toxic as their parent compound. Screening levels are available for these degradation products (see Appendix F). Of the other chemical warfare agents evaluated in this report, only agent VX degrades to a toxic and potentially persistent compound, S-(Diisopropylaminoethyl) methylphosphonothioate (EA-2192). The HBESLs derived for VX can also be used for this compound (see Appendix F). In the cases of Lewisite and VX, assessments for the presence of breakdown compounds Lewisite oxide and inorganic arsenic (for Lewisite) and EA-2192 (for VX) are warranted due to their particular toxicity and potentially significant persistence. Other likely breakdown products such as thiodiglycol from HD, and methylphosphonic acid (MPA) from the G-agents and VX, do not pose a significant health risk. However, due to their persistence in the environment, they may be useful indicators of historical chemical warfare agent presence.

11.3.4 It is unlikely that the chemical agents addressed in this document will contaminate ground water. Site-specific evaluations are recommended to identify those circumstances where potential ground-water contamination should be evaluated. It is also unlikely that these agents would contaminate a drinking water source. Site-specific assessment should be conducted only for those circumstances where contamination of a drinking water source is a realistic concern.

11.3.5 Other applications of these models may be an appropriate mechanism to assess other scenarios where there is potential for long-term or repeated exposures (such as for waste management or when assessing nonpervious contaminated surfaces). For these potential applications of chronic risk assessment models, common generic assumptions do not currently exist. Evaluating risks in these scenarios is the subject of potential future initiatives.

11.4 KEY UNCERTAINTIES ASSOCIATED WITH THE CHEMICAL WARFARE AGENT HBESLs

Uncertainties within the assessment process can result in either an overconservative (e.g., the HBESL concentration may actually be lower than a level that will protect public health) or underconservative (e.g., the HBESL may not be low enough to ensure protection of public health). Several areas of uncertainty were identified during the evaluation of these screening level methodologies. This is typical of input parameters for which there is limited information or which represent general theoretical scenarios as opposed to a specific site. Even for parameters with sufficient data, it is sometimes necessary to use professional judgement based on experience to determine which are best for a particular situation. In this evaluation, the uncertainties are not necessarily specific to the calculation of screening levels for *chemical warfare agents*, but also span a variety of data gaps and generalizations that are also imparted to screening levels that are established for commercial chemical compounds. This section summarizes some of the major data gaps - both general and chemical agent specific.

The uncertainties begin with the actual models (or mathematical algorithms) currently used in the environmental risk assessment process; in particular on the issue of how accurately such models describe the process of exposure from a source. The other uncertainties are associated with the assumptions that go into these models. Overall, the types of uncertainty may be broken down into three general

categories: 1) model uncertainty, 2) exposure uncertainty, and 3) toxicity data uncertainty.

Examples of model uncertainties include whether or not all pathways should result in an additive exposure or whether pathways appropriately represent real-world processes. Exposure parameter uncertainties include the variability or unknown aspects of exposure. Parameters such as exposure frequency and duration are primary examples of parameters which may have a significant impact on the resulting calculated values, but for which it is inherently difficult to determine how accurately the assumed value represents a true occurrence. The chronic toxicity values are extremely important to the overall estimation of risk or calculated screening level value. Several uncertainties such as human variability, extrapolation from animal data, and extrapolation of acute or subchronic data to estimate a chronic threshold are just a few examples of the many assumptions that must be accounted for in the development of the values used in the risk assessment model. Overall, the balance of uncertainty in the calculation is designed to 'err' on the side of conservatism.

Ascertaining the degree and overall effect/impact of the uncertainty associated with a calculated screening level cannot be done quantitatively. However, a qualitative evaluation provides essential information to consider when using such screening levels as a decision-tool. Various uncertainties associated with the models themselves, as well as with the individual input parameter assumptions, have been described in detail throughout this document. Additional uncertainties associated with the application of the models to less common scenarios are summarized in the individual unique scenario example appendices. Some of the key uncertainties and their effects on the HBESLs associated with the scenarios described in the main text of this document are summarized in Table 11-1.

Table 11-1. Key Areas of Uncertainty and Effect on Conservatism of HBESL

Type of Uncertainty	Discussion	Effect On Conservatism of HBESL[a]
Single Pathway Models - RBCs, SSLs	For the nerve agents (GA, GB, GD, and VX) the use of these models may underestimate risk by only addressing single exposure pathways (assuming cumulative effects even through different routes of exposure)	↓
	For the vesicants (HD and Lewisite), the effects may not be the same if introduced through different routes of exposures; may be most appropriate	↕
Multipathway Model - PRG	For the nerve agents (GA, GB, GD, and VX) the use of this model seems the most justifiable in that it sums the total effects on the body (assuming same effects even through different routes of exposure)	↕

Table 11-1. Key Areas of Uncertainty and Effect on Conservatism of HBESL		
	For the vesicants (HD and Lewisite), the effects may not be the same if introduced through different routes of exposures; adding all pathways may be slightly overconservative	↑
Environmental degradation	Natural degradation processes such as photo degradation and environmental half-life were not included in the concepts of the chronic risk model - rather a continued long-term exposure to these concentrations is assumed even though this situation may not be reasonably expected under most environmental conditions.	↑
Toxicity endpoints	Noncancer chemical agent RfDs; peer-reviewed chronic life-time dose estimates currently under review by NRC, COT but approved by DA OTSG for interim use - believed to be conservative estimates	↕
	Cancer slope factor for HD; Recent study by Gaylor (1998) indicated that the CSF for HD ranges from 1.6 to 9.5 $mg/kg/day^{-1}$. To be conservative, USEPA's proposed value of 95 $mg/kg/day^{-1}$ was also included to derive a geometric mean for HD CSF.	↑
Organic carbon partition coefficient (K_{oc})	This parameter was estimated by using a regression relationship based on each chemical agent's octanol-water partition coefficient (K_{ow}). Actual experimental values may be different for each chemical agent.	↕
Soil water partition coefficient (K_d)	The K_d was estimated from the chemical's K_{oc} and by assuming a soil organic carbon content. Actual site-specific value may differ depending on the organic carbon content.	↕
Exposure duration (ED)	USEPA default exposure durations were used for each of the exposure scenarios. The length of time an individual resides at a location may vary; however, the defaults are conservative for the specified scenarios in the main document	↑
Skin surface area (SA)	Default SAs were used and assumed to be reasonably conservative for the given scenarios. However, this parameter may be significantly impacted by individual variation, clothing, temporal, and seasonal factors.	↕
Exposure frequency (EF)	USEPA default values were used for the scenarios presented in the main portion of this document. The EF may vary between individuals; however; the defaults are conservative for the specified scenarios in the main document.	↑

Table 11-1. Key Areas of Uncertainty and Effect on Conservatism of HBESL		
Soil-to-skin adherence factor (AF)	Site-specific soil data may indicate that this parameter is higher or lower than the USEPA default.	↕
Dermal absorption factor	An organic carbon content of 2% was assumed for the purpose of estimating dermal absorption from the soil. Actual organic carbon content can vary from site to site.	↕
	The absorption factor is assumed to be constant over the total period of exposure (8 and 12 hours).	↑
GI absorption factor	Dermal toxicity values were extrapolated from each chemical agent's oral toxicity value. Due to lack of chemical-specific GI absorption factors, a default GI of 100% was assumed. Actual GI absorption factors may be lower.	↓

[a] ↑: uncertainty results in an overconservative HBESL
↓: uncertainty results in an underconservative HBESL
↕: effect on conservatism of HBESL may vary

11.5 RECOMMENDATIONS

The Table below lists HBESL values for two common generic scenarios using three current EPA chronic risk assessment methods, common default and chemical-specific parameters. The information in this document can be used to help stakeholders determine if screening levels can be used, and if so, what models and parameters best fit site-specific needs. The HBESLs can be used as action/no-action determinants ('action' meaning to perform site-specific health risk assessment; apply management controls; treat/remediate; or a combination of these) when assessing the potential for chronic health effects to exposed populations so long as the following conditions are met:

11.5.1 *Levels of risk are acceptable to the situation (see Section 1.3.2).* This can only be assessed through negotiation with applicable regulators and other stakeholders.

11.5.2 *Assumptions made in these scenarios are at least equally conservative, if not more conservative, than site-specific values.* For example, if the exposure to persons in a hypothetical industrial scenario is anticipated to be less than 100 days/yr, the HBESL exposure frequency assumption of 250 days/yr is more conservative; therefore allowing for a conservatively 'safe' screening decision.

11.5.3 *Substance concentrations and exposure assumptions are not expected to be acutely toxic (see Section 1.3.8).* For scenarios involving limited exposure duration and frequency values, these models should be used only with extreme caution. In certain cases the application of these chronic risk assessment models may be inappropriate and acute toxicity to short-term exposures should be evaluated separately.

11.5.4 *A single chemical is of concern (see Section 1.3.9).*

11.5.5 *Ground-water contamination is not considered to be a concern (see Appendix E).*

11.5.6 *Risk to ecological receptors is not expected (see Section 1.3.10).* HBESLs listed in this document do NOT address ecological risk, and may not be sufficiently conservative to protect all ecological receptors at all sites.

Table 11-2. Range of Estimated HBESL Values for Chemical Warfare Agents

	Residential soil (mg/kg)			Industrial soil (mg/kg)		
	RBCs	PRGs	SSLs	RBCs	PRGs	SSLs
HD	0.55	0.01[a]	0.016	14	0.3[a]	NA
Lewisite[c]	7.8	0.3	7.8	(7.8)[d]	3.7	NA
GA	3.1	2.8	0.8	82	68	NA
GB	1.6	1.3	0.5	41	32	NA
GD	0.31	0.22	0.18	8.2	5.2	NA
VX[b]	0.047	0.042	0.047	1.2	1.1	NA

[a] Cancer-based; residential target risk level of 10^{-5}, industrial target risk level of 10^{-4}

[b] Assessment should include EA-2192, a particularly toxic and relatively persistent breakdown component of VX. Due to similar toxicity, the HBESLs derived for VX can be used for EA-2192.

[c] Assessment should include CVA/Lewisite oxide & arsenic, persistent breakdown products of Lewisite. USEPA screening levels for inorganic arsenic should be consulted. HBESLs for Lewisite can be used for CVA and Lewisite oxide.

[d] RBC value derived for the commercial/industrial scenario was potentially above acute toxicity levels, therefore the upper bound value of the residential scenario is suggested as a substitute.

12. REFERENCES

AIHC (American Industrial Health Council). 1994. *Exposure Factors Sourcebook*. American Industrial Health Council, Washington, DC.

Andelman, J.B. 1990. Total exposure to volatile organic chemicals in potable water. In: *Significance and Treatment of Volatile Organic Compounds in Water Supplies*, N.M. Ram, R.F. Christman, and K.P. Cantor, eds. Lewis Publishers, Boca Raton, FL.

Anderson, E.L. 1983. Quantitative approaches in use to assess cancer risks. *Risk Analysis* 3:277-295.

ATSDR. 1993. Update, Toxicological Profile for Arsenic. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Disease Registry.

Baker, D.J. and E.M. Sedgwick. 1996. Single fibre electromyographic changes in man after organophosphate exposure. *Hum. Exp. Toxicol.* 15:369-375.

Bramwell, E.C., W.S. Ladell and R.J. Shepard. 1963. *Human Exposure to VX.* Porton Technical Paper No. 830. Directorate of Chemical Defense Research and Development, Porton Down, UK.

Britton, K.B. and C.L. Grant. 1988. *Prediction of Octanol-Water Partition Coefficients of Organophosphates. Evaluation of structure-function relationships.* Special Report 88-11, U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory, Hanover, NF.

CDC (Centers for Disease Control). 1990. *Results of a Workshop Meeting to Discuss Protection of Public Health and Safety During Reentry into Areas Potentially Contaminated with a Lethal Chemical Agent (GB, VX or Sulfur Mustard).* Draft report, July 6, 1990, Centers for Disease Control, U.S. Public Health Service.

Cowherd, C., G. Muleski, P. Engelhart and D. Gillette. 1985. *Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination.* EPA/600/8-85/002. Prepared for the Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, Washington, DC.

Craig, F.N., E.G. Cumming and V.M. Sim. 1977. Environmental temperature and the percutaneous absorption of a cholinesterase inhibitor, VX. *J. Invest. Dermatol.* 68:357-361.

Culp, S.J., D.W. Gaylor, W.G. Sheldon, L.S. Goldstein and F.A. Beland. 1997. A comparison of the tumors induced by coal tar and benzo[a]pyrene in a 2-year bioassay. *Carcinogenesis* 19:117-124.

DA (Department of the Army). 1974. *Chemical Agent Data Sheets*, Edgewood Arsenal Special Report, EO-SR-74001. Department of the Army, Edgewood Arsenal, Aberdeen Proving Ground, MD.

DA (Department of the Army). 1986. *Occupational and Environmental Health Sanitary Control and Surveillance of Field Water Supplies*, TB MED 577, Headquarters, Department of the Army, Washington, DC.

DA (Department of the Army). 1988. *Final Programmatic Environmental Impact Statement for the Chemical Stockpile Disposal Program*, Office of the Program Executive Officer, Program Manager for Chemical Demilitarization. Aberdeen Proving Ground, MD.

DA (Department of the Army). 1990. *Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Nerve Agents GA, GB. GD, and VX*, Pamphlet 40-8, Headquarters, Department of the Army, Washington, DC.

DA (Department of the Army). 1991. *Occupational Health Guidelines for the Evaluation and Control of Occupational Exposure to Mustard Agents H, HD, and HT*, Pamphlet 40-173, Headquarters, Department of the Army, Washington, DC.

DA (Department of the Army) 1992. *Material Safety Data sheets: HD and THD*. U.S. Department of the Army, Edgewood Research Development and Engineering Center, APG, MD.

DA (Department of the Army). 1993. *Memorandum: Fact Sheets for Contaminants of Concern and Estimated Soil Levels for Closure*. HSDB-ME-SR (40), Jan. 12, 1993.

DA (Department of the Army). 1996a. *Interim Chronic Toxicological Criteria for Chemical Warfare Compounds*. Memorandum MCHB-DC-C, dated June 4, 1996. Department of the Army, Office of the Surgeon General, Falls Church, VA.

DA (Department of the Army). 1996b. *Occupational and Environmental Health Sanitary Control and Surveillance of Field Water Supplies*, Draft revision. TB MED 577, Headquarters, Department of the Army, Washington, DC. (in review)

Dacre, J.C. 1984. *Recommended interim criteria for three environmental polluting compounds from Rocky Mountain Arsenal*. NTIS/AD-A154826/2.

DHHS (Department of Health and Human Services, Centers for Disease Control). 1988. Final recommendation for protecting the health and safety against potential adverse effects of long-term exposure to low doses of agents GA, GB, VX, mustard agent (H, HD, T), and Lewisite (L). *Federal Register* 53: 8504 (March 15, 1988).

DHHS (Department of Health and Human Services, Centers for Disease Control and Prevention). Letter to Veronique Hauschild, USACHPPM, dated January 15, 1997, signed by Paul Joe, Special Programs Group, National Center for Environmental Health, CDC, Atlanta, GA.

Forsman, N, H. Frostling, O. Hertzberg, et al. 1979. *C-Weapons (Characteristics and Defense)*. USAMIIA-HT-010-79. US Army Medical Intelligence and Information Agency. Fort Detrick, MD. (as cited in MacNaughton and Brewer, 1994)

Fowler, W.K., D.C. Stewart and D.S. Weinberg. 1991. Gas chromatographic determination of the lewisite hydrolysate, 2-chlorovinylarsonous acid, after derivatization with 1,2-ethanedithiol. *Jr. Chromatograph*. 558:235-246.

Freeman, G., F.N. Marzulli, A.B. Craig and J.R. Trimble. 1954. *The Toxicity of Liquid GA Applied to the Skin of Man*. Chemical Corps Medical Laboratory Research Report No. 250. Army Chemical Center, MD.

Gaylor, D. 1998. *Carcinogenic Potency for Sulfur Mustard. Memo dated March 11, 1998, to V. Hauschild, Army Environmental Center, and Veronique Hauschild, Army Center for Health Promotion and Preventive Medicine*. National Center for Toxicological Research, Jefferson, AR.

Gaylor, D. and L.S. Gold. 1995. Quick estimate of the regulatory virtually safe dose based on the maximum tolerated dose for rodent bioassays. *Regul. Toxicol. Pharmacol.* 22:57-63.

Graham, J.D. 1993. The legacy of one in a million. *Risk in Perspective* 1:1-2.

Grob D., and J.C. Harvey. 1958. Effects in man of the anticholinesterase compound Sarin (isopropyl methyl phosphonofluoridate). *J. Clin. Invest.* 37(1):350-368.

Grob, D., B. Zeigler, G. Saltzer and G.I. Johnston. 1953. Further observations on the effects in man of methyl isopropyl flurorophosphonite (GB): effects of percutaneous absorption through intact and abraded skin. Chemical Corps Medical Laboratories Contract Report, MLCR No. 14. Johns Hopkins University, Baltimore, MD.

Hackett, P.L., R.L. Rommereim, F.G. Burton, R.L. Buschbom, and L.B. Sasser. 1987. *Teratology studies on lewisite and sulfur mustard agents: effects of sulfur mustard in rats and rabbits*. DTIC: AD A187495. Pacific Northwest Laboratory, Richland, WA. Prepared for the U.S. Army Medical Research and Development Command, Fort Detrick, MD.

Henriques, F.C., A.R. Moritz, H.S. Breyfogle and L.A. Patterson. 1944. *The mechanism of cutaneous injury by mustard gas. An experimental study using mustard prepared with radioactive sulfur.* OSRD 3620. National Defense Research Committee of the Office of Scientific Research and Development. (Cited in Craig et al., 1977)

Henry, M. 1991. *Literature Review of Sulfur Mustard Toxicity*. USAMRICD-TR-91-01, January, 1991. (as cited by Reutter, 1998)

Howard, P.H. and W.M. Meylan. 1997. *Handbook of Physical Properties of Organic Chemicals* CRC Lewis Publishers, Boca Raton, FL.

IARC (International Agency for Research on Cancer). 1987. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man: Overall Evaluation of Carcinogenicity: An Updating of IARC Monographs Volumes 1-42*, Suppl. 7, p. 67. International Agency for Research on Cancer, Lyons, France.

ICRP (International Commission on Radiological Protection). 1981. *Report of the Task Group on Reference Man*. Pergamon Press, New York.

James M. Montgomery, Consulting Engineers, Inc. (1987). Ground-Water Quality Assessment Engineering Report, Tooele Army Depot, Utah. Salt-Lake City, Utah.

Kelly, K.E. 1991. "The myth of 10^{-6} as a definition of acceptable risk, or in hot pursuit of the holy grail." Paper presented at the 84th Annual Meeting of the Air and Waste Management Association, Vancouver, BC. (as cited in *Underground Tank Technology Update*, 1996, vol. 10:4-6)

Kimura, K.K., B.P. McNamara and V.M. Sim. 1960. *Intravenous Administration of VX in Man.* CRDLR 3017. U.S. Army Chemical Research and Development Laboratories, Army Chemical Center, MD

King, J.W. and H.A. Brown. 1994. Aspects of Partition Coefficient Estimation in Agent Research. Proc. ERDEC Scientific Conference on Chemical Defense Research. Nov. 16-19, 1993.

Landahl, H.D. 1945. *A Formal Analysis of the Action of Liquid Vesicants on Bare Skin.* University of Chicago Toxicity Laboratory Report No. 50. U. of Chicago, Chicago, IL.

Lohner, T.W. 1997. Is 10^{-6} an appropriate *de minimis* cancer risk goal? *Risk Policy Report*, April 18, 1997, pp. 31-33.

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt. 1982. *Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds.* McGraw-Hill Book Co., New York

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. *J. Phys. Chem. Re. Data* 7:383-415.

MacNaughton, M.G. and J.H. Brewer. 1994. *Environmental Chemistry and Fate of Chemical Warfare Agents.* Final Report, prepared for the Army Corps of Engineers, Southwest Research Institute, San Antonio, TX

Major, M. 1997. *Estimation of the dermal absorption of the chemical agents from a soil matrix.* Memorandum dated March 24, 1997, to V. Hauschild, U.S. Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, MD

Major, M. 1998. Memorandum for MCHB-TS-EHRARCP (Aug 5 1998)

Manthei, J.H., J.M. Klein, W.C. Heyl, D.H. Heitkamp, R.D. Moore, and R.A. Braun. 1983. *Toxicological Evaluation of Mustard (HD) and Thickened Mustard (THD) Contact and Vapor Hazard in Rabbits.* Technical Report ARCSL-TR-83040. U.S. Army Armament, Munition and Chemical Command, Aberdeen Proving Ground, MD.

Manthei, J.H., D.H. Heitkamp, W.C. Starke, R.A. Braun, R.E. Herd, D.M. Bona, R.D. Moore, K.P. Cameron, and W.C. Heyl. 1985. *Toxicological Evaluation of the Contact and Vapor Hazards of VX and Thickened VX in Rabbits.* Technical Report CRDC-TR-84072. U.S. Army Armament, Munition and Chemical Command, Aberdeen proving Ground, MD.

Manthei, J.H., D.H. Heitkamp, R.W. Dorsey, R.A. Braun, D.M. Bona, R.D. Moore, K.P. Cameron, and J.M. Klein. 1986. *Toxic Hazard to the Rabbit from Direct and Vapor Contact with HD-Contaminated Plexiglas, Concrete, or XM40 Nylon Carrier Material.* Technical Report CRDC-TR-86072. U.S. Army Armament, Munition and Chemical Command, Aberdeen proving Ground, MD.

Manthei, J.H., D.H. Heitkamp, R.W. Dorsey, W.C. Starke, D.M. Bona, R.D. Moore, and K.P. Cameron. 1988. *Mustard Contact Toxic Hazard, Correlation of the Effects in Skin with Contamination Levels Recovered from Dental Dam and Painted Steel Surfaces. 1. Animal and Chemical Data.* Technical Report CRDC-TR-88142. U.S. Army Armament, Munition and Chemical Command, Aberdeen proving Ground, MD.

Marzulli, F.N. and M.R. Williams. 1953. *Studies on the Evaporation, Retention and Penetration of GB Applied to Intact Human and Intact and Abraded Rabbit Skin.* CMLRE-ML-52. Chemical Corps Medical Laboratory, Army Chemical Center, MD.

McKee, W.H.E. and B. Woolcott. 1949. *Report on Exposures of Unprotected Men and Rabbits to Low Concentrations of Nerve Gas Vapour.* PRP-143. Chemical Defence Establishment, Porton Down, UK.

McNamara, B.P., F. Leitnaker and F.J. Vocci. 1973. *Proposed Limits for Human Exposure to VX Vapor in Nonmilitary Operations.* EASP 1100-1 (R-1) (DTIC: AD 770434/9). U.S. Department of the Army, Medical Research Laboratory, Edgewood Arsenal, Aberdeen Proving Ground, MD.

McNamara, B.P., E.J. Owens, M.K. Christensen et al. 1975. *Toxicological Basis for Controlling Levels of Mustard in the Environment.* EASP EBSP 74030. U.S. Department of the Army, Biomedical Laboratory, Edgewood Arsenal, Aberdeen Proving Ground, MD.

Mioduszewski, R.J., S.A. Reutter, L.L. Miller, E.J. Olajos and S.A. Thomson. 1998. *Evaluation of Airborne Exposure Limits for G-Agents: Occupational and General Population Exposure Criteria.* ERDEC-TR-489. Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, MD.

Munro, N, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J. King, and V. Hauschild. The Sources, Fate, and Toxicity of Chemical Warfare Agent Breakdown Products. Submitted to *Environ. Health Perspectives* in December 1998.

NRC (National Research Council). 1995. *Guidelines for Chemical Warfare Agents in Military Field Drinking Water.* Subcommittee on Guidelines for Military Field Drinking Water Quality, Committee on Toxicology, National Research Council, National Academy Press, Washington, DC.

NTP (National Toxicology Program). 1997. *Annual Report on Carcinogens* (online file). National Toxicology Program. Research Triangle Park, NC.

Omenn, G.S., S. Stuebbe and L.B. Lave. 1995. Predictions of rodent carcinogenicity testing results: interpretation in light of the Lave-Omenn value-of-information model. *Molec. Carcinogen.* 14:37-45.

Opresko, D. M., M.L. Daugherty, E. Etnier, R. Faust, S. Talmage, R. Young, A. Watson, A, Ross. 1994. *Estimated Control Limits, Technologies and Regulatory Requirements for Remediating Sites Potentially Contaminated with Nonstockpile Chemical Materiels.* Draft Report. Oak Ridge National Laboratory, Oak Ridge, TN

Opresko, D. M., R. Young, S. Talmage, R. Faust, A. Watson, A, Ross, K. Davidson and J. King. 1998. Chemical warfare agents: estimating oral reference doses. *Reviews of Environmental Contamination and Toxicology* 156:1-183.

Papirmeister, B., A.J. Feister, S.I. Robinson and R.D. Ford. 1991. *Medical Defense Against Mustard Gas: Toxic Mechanisms and Pharmacological Implications.* CRC Press, Boca Raton, FL.

Pease, W.S., L. Zeise and A. Kelter. 1990. Risk assessment for carcinogens under California's Proposition 65. *Risk Analysis* 10:255-271.

Ravi, V. and J.A. Johnson (1996). *VLEACH- a one dimensional finite difference vadose zone leaching model.* Version 2.0. With supplement for Version 2.2a. Publication of Dynamic Corporation available at http://earth1.epa.gov/ada/models.html.

Reutter, S.A., E.J. Olajos, R.J. Mioduszewski and A. Watson. 1994. *White Paper - Validation of Contact Hazard Toxicity Estimates for Agents VX and HD, Phase II.* ERDEC-SP-017. Edgewood Research Development Engineering Center, U.S. Army Chemical and Biological Defense Command, Aberdeen Proving Ground, MD.

Reutter, S.A. and J.V. Wade. 1994. *Review of Existing Toxicity Data and Human Estimates for Selected Chemical Agents and Recommended Human Toxicity Estimates Appropriate for Defending the Soldier.* ERDEC-SP-018. Edgewood Research Development Engineering Center, U.S. Army Chemical and Biological Defense Command, Aberdeen Proving Ground, MD. CLASSIFIED REPORT (as cited by Reutter, 1998)

Reutter, S.A. 1998. Comments on the proposed Health-based Environmental Screening Levels (HBESLs). Memo to V. Hauschild, U.S. Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, MD.

Rice, G.B., T.W. Lambert, B. Haas and V. Wallace. 1971. *Effect of Chronic Ingestion of VX on Ovine Blood Cholinesterase.* DTC 71-512. Deseret Test Center, Dugway Proving Ground, Dugway, UT.

Rodricks, J.V., S.M. Brett and G.C. Wrenn. 1987. Significant risk decisions in federal regulatory agencies. *Reg. Toxicol. Pharmacol.* 7:307-320.

Rosenblatt, D.H., T. A. Miller, J.C. Dacre, I. Muul and D.R. Cogley. 1975. *Problem Definition Studies on Potential Environmental Pollutants*, Technical Report 7509. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, MD.

Rosenblatt, D.H., M.J. Small, T.A. Kimmell and A.W. Anderson. 1995. *Agent Decontamination Chemistry, Draft Technical Report.* Environmental Quality Office, U.S. Army Test and Evaluation Command, Deseret Test Center, Fort Douglas, UT.

Rosenbloom, J., P. Mock, P. Lawson, J. Brown, and H.J. Turin. (1993) *Application of VLEACH to Vadose Zone Transport of VOCs at an Arizona Superfund Site.* Ground Water Monitoring and Remediation 13: 159-169.

Rouhi, A.M. 1998. Buzzing patrols. *Chem. Eng. News*, May 26, 1998.

RTECS (Registry of Toxic Effects of Chemical Substances). 1997. Online file retreived September 18, 1997. National Institute for Occupational Safety and Health, Cincinnati, OH.

Sage, G.W. and P.H. Howard. 1989. *Environmental Fate Assessments of Chemical Agents HD and VX.* CRDEC-CR-034. U.S. Army Armament Munitions Chemical Command, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD.

Sample, B.E., D.M. Opresko and G.W. Suter, III. 1996. *Toxicological Benchmarks for Wildlife*: 1996 Revision. ES/ER/TM-86/R3. Oak Ridge National Laboratory, Oak Ridge, TN.

Sasser, L.B., R.A. Miller, D.R. Kalkwarf, et al. 1989a. *Toxicology Studies on Lewisite and Sulfur Mustard Agents: Two-generation reproduction study of sulfur mustard (HD) in rats.* PNL 6944 (DTIC: AD A216423). Pacific Northwest Laboratories. Prepared for the U.S. Army Medical Research and Development Command, Fort Detrick, MD.

Sasser, L.B., J.A. Cushing, D.R. Kalkwarf, P.W. Mellick and R.L. Buschbom. 1989b. *Toxicology Studies of Lewisite and Sulfur Mustard Agents: Two-generation reproduction study of lewisite in rats.* PNL-6978. Pacific Northwest Laboratories, Richland, WA.

Sasser L.B., R.A. Miller, D.R. Kalkwarf, et al. 1996. Subchronic toxicity evaluation of sulfur mustard in rats *J. Appl. Toxicol.* 16:5-13.

Sidell, F.R. and W.A. Groff. 1974. The reactivatibility of cholinesterase inhibited by VX and Sarin in man. *Toxicol. Appl. Pharmacol.* 27:241-252.

Sim, V.M. 1962. *Variability of Different Intact Human Skin Sites to the Penetration of VX.* CRDLR 3122. Chemical Research and Development Laboratories, Army Chemical Center, MD.

Small, M.J. 1984. *Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate.* Technical Report 8304. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

State of Utah, Department of Natural Resources (1981). Information Bulletin No. 26: Test Drilling For Fresh Water in Tooele Valley, Utah.

Suter, G.W., III and C.L. Tsao. 1996. *Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota.* 1996 Revision. ES/ER/TM-96/R2. Oak Ridge National Laboratory, Oak Ridge, TN.

Szafraniec, L.J., L.L. Szafraniec, W.T. Beaudry, et al. 1990. *On the Stoichiometry of Phosphonothiolate Ester Hydrolysis.* CRDEC-TR-212. U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD. (as cited in Rosenblatt et al., 1995)

Talmage, S.S., et al. 1999. *Nitroaromatic Munitions Compounds: Environmental Effects and Screening Values.* Reviews in Environmental Contamination and Toxicology. Vol 161:1 - 156

Travis, C.C. et al. 1987. Cancer risk management: a review of 132 federal regulatory agencies. *Environ. Sci. Technol.* 21:415-420.

USACHPPM, Memorandum for Record, subj: Minutes of Meeting on VX Health Criteria Document; November 1998, Environmental Risk Assessment and Risk Communication Program.

USEPA. 1984. *An Estimation of the Daily Food Intake Based on Data from the 1977-1978 USDA Nationwide Food Consumption Survey.* EPA/520/1-84/021. Office of Radiation Protection, Washington, DC.

USEPA. 1985. *Development of Statistical Distributions or Ranges of Standard Factors Used in Exposure Assessments.* EPA/600/8-85/010. Office of Health and Environmental Assessment, Washington, DC.

USEPA. 1989a. *Exposure Factors Handbook.* EPA-600/8-89/043. Office of Health and Environmental Assessment, Office of Research and Development, Washington, DC. NTIS PB90-106774/AS.

USEPA. 1989b. *Risk Assessment Guidance for Superfund: Volume 1 Human Health Evaluation Manual (Part A).* EPA/540/1-89/002. Office of Emergency and Remedial Response, Washington, DC.

USEPA. 1991a. *Risk Assessment Guidance for Superfund: Volume 1 Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals).* Publication 9285.7-01B. Office of Emergency and Remedial Response, Washington, DC.

USEPA. 1991b. *Upper-bound Quantitative Cancer Risk Estimate for Populations Adjacent to Sulfur Mustard Incineration Facilities.* EPA/600/8-91/053. Office of Research and Development, U.S. Environmental Protection Agency, Washington, DC.

USEPA. 1992. *Dermal Exposure Assessment: Principles and Applications.* EPA/600/8-91/011B. Office of Health and Environmental Assessment, Washington, DC.

USEPA. 1993. *Health Advisories for Drinking Water Contaminants.* Office of Water, Washington, DC, Lewis Publishers, Boca Raton, FL

USEPA. 1994a. *Air Emissions Models for Waste and Wastewater.* EPA-453/R-94-080A. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

USEPA. 1994b. *Methods for the Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry.* EPA/600/8-90/066F. Office of Research and Development, Washington, DC.

USEPA. 1995a. *Assessing Dermal Exposure from Soil.* EPA Region III, Technical Guidance Manual. December 1995. EPA Contact: Jennifer Hubbard, EPA Region III, Office of Superfund Programs, Philadelphia, PA.

USEPA. 1995b. *Supplemental Guidance to RAGs: Region IV Bulletins, Human Health Risk Assessment.* Waste Management Division, Atlanta GA.

USEPA. 1996a. *EPA Region III Risk-Based Concentration Table, Background Information. Development of Risk-Based Concentrations.* April 30, 1996. EPA Contact: Roy L. Smith, EPA Region III, Office of Superfund Programs, Philadelphia, PA. (online file at http://www.epa.gov/reg3hwmd/risk/guide4.htm, retrieved March 31, 1997).

USEPA. 1996b. *EPA Region IX Preliminary Remediation Goals (PRGs),* August 1, 1996. EPA Contact: Standford J. Smucker, EPA Region IX, San Francisco, CA.

USEPA. 1996c. *Soil Screening Guidance: Users Guide.* EPA/540/R-96/018, Office of Solid Waste and Emergency Response, Washington, DC.

USEPA. 1996d. *Soil Screening Guidance: Technical Background Document.* EPA/540/R-95/128, Office of Emergency and Remedial Response, Washington, DC.

USEPA. 1996e. *Proposed Guidelines for Ecological Risk Assessment.* Notice of Availability and Opportunity to Comment on Proposed Guidelines for Ecological Risk Assessment. Federal Register 61:47552-47631.

USEPA. 1997a. *Integrated Risk Information System (IRIS).* Online file. Office of Research and Development, National Center for Environmental Assessment, Cincinnati, OH.

USEPA. 1997b. *EPA Region III Updated Risk-Based Concentration Table.* March 17, 1997. EPA Region III, Office of Superfund Programs, Philadelphia, PA.

USEPA. 1997c. *Health Effects Assessment Summary Tables.* National Center for Environmental Assessment, U.S. Environmental Protection Agency, Cincinnati, OH.

USEPA. 1997d. *Exposure Factors Handbook.* EPA-600/P-95/002Fa. National Center for Environmental Assessment, Office of Research and Development, Washington, DC.

USEPA. 1998. *Region IX PRGs*, May 1, 1998. http://www.epa.gov/region09/waste/sfund/prg/intro.htm. EPA Contact: Standford J. Smucker, EPA Region IX, San Francisco, CA.

U.S. Geological Survey (1996). Water-Resources Investigations Report 95-4248: Hydrologic Setting, Hydraulic Properties, and Ground-water Flow at the O-field Area of Aberdeen Proving Ground, Maryland.

van Hooidonk, C, B.I. Ceulen, H. Kienhuis and J. Bock. 1980. Rate of penetration of organophosphates in diffusion cells. In: *Mechanisms of Toxicity and Hazard Evaluation.* Elsevier/North Holland Biomedical Press.

Verweij, A. and H.L. Boter. 1976. Degradation of *S*-2-di-isopropylaminoethyl *O*-ethyl methylphosphonothioate in soil: Phosphorus-containing products. *Pest. Sci.* 7:355-362.

WHO (World Health Organization). 1984. *Guidelines for drinking water quality.* WHO, Geneva.

Watson, A.P., T.D. Jones and G.D. Griffin. 1989. Sulfur mustard as a carcinogen: application of relative potency analysis to the chemical warfare agents H, HD, and HT. *Reg. Toxicol. Pharmacol.* 10:1-25.

Williams, R.T., W.R. Miller and A.R. MacGillivray. 1987. *Environmental Fate and Effects of Tributyl Phosphate and Methyl Phosphonic Acid.* NTIS/AD-A184 959/5.

Yang, Y-C., L.L. Szafraniec, W.T. Beaudry and D.K. Rohrbaugh. 1990. Oxidative detoxification of phosphonothiolates. *J. Amer. Chem Soc.* 112:6621-6627. (as cited in Rosenblatt et al., 1995)

GLOSSARY

ABS_{derm}: Dermal Absorption Factor

ABS_{gi}: Gastrointestinal Absorption Factor

Absorbed Dose: The amount of a substance penetrating the exchange boundaries of an organism after contact. Absorbed dose is calculated from the intake and the absorption efficiency. It usually is expressed as mass of a substance absorbed into the body per unit body weight per unit time (e.g., mg/kg-day).

Absorption: The penetration of a substance into or through another substance or medium. The uptake and entry of a substance through intact skin, eyes, gastrointestinal tract or lungs (i.e., ingestion or once the substance has entered the lungs).

Acetylcholinesterase: A member of the cholinesterase group of enzymes that is naturally present at nerve endings and in red blood cells and which normally breaks down acetylcholine into acetic acid and choline; an enzyme that is inhibited by nerve agents.

Adsorption: The adhesion of a substance to the surface of another solid or liquid (not to be confused with absorption).

Adverse Effect Level (AEL): An exposure level at which there are statistically or biologically significant increases in frequency or severity of deleterious effects between the exposed population and its appropriate control group.

AF_a: Soil-to-Skin Adherence Factor for adult

AF_c: Soil-to-Skin Adherence Factor for child

Agent GA: The chemical ethyl N,N-dimethylphosphoramidocyanidate, Chemical Abstracts Service (CAS) registry number 77-81-6, in pure form and in the various impure forms found in military storage as well as in military industrial, depot, or laboratory operations (synonym = Tabun); a nerve agent with chemical formula $C_5H_{11}N_2O_2P$.

Agent GB: The chemical isopropyl methylphosphonofluoridate, CAS number 107-44-8, in pure form and in the various impure forms found in military storage as well as in military industrial, depot, or laboratory operations (synonym = Sarin); a nerve agent with chemical formula $C_4H_{10}FO_2P$.

Agent GD: The chemical pinacolyl methyl phosphonofluoridate, CAS number 96-64-0, in pure form and in the various impure forms found in military storage as well as in military industrial, depot, or laboratory operations (synonym = Soman); a nerve agent with chemical formula $C_7H_{16}FO_2P$.

Agent H: Levinstein mustard; a mixture of 70 percent bis(2-chloroethyl) sulfide, CAS # 505-60-2, and 30 percent sulfur impurities produced by the Levinstein process. Agent H is a blister agent and is unstable.

Agent HD: Distilled mustard or bis(2-chloroethyl) sulfide, CAS registry number 505-60-2. Distilled mustard (HD) is mustard (H) that has been purified by washing and vacuum distillation to reduce sulfur impurities; a blister agent with chemical formula $C_4H_8Cl_2S$.

Agent HT: A plant-run mixture containing about 60 percent HD and <40 percent agent T plus a variety of sulfur contaminants and impurities. Agent T is bis [2-(2-chloroethylthio)ethyl]ether, CAS registry number 63918-89-8, and is a sulfur, oxygen and chlorine compound similar in structure to HD (Agent T has chemical formula $C_8H_{16}Cl_2OS_2$). Agent HT is a blister agent with a lower freezing point than agent HD.

Agent L, or Lewisite: 2-chlorovinyldichloroarsine, CAS registry number 541-25-3; agent L is a blister agent with the chemical formula $C_2H_2AsCl_3$.

Agent VX: The chemical O-ethyl S-(2-diisopropylaminoethyl)methylphosphonthioate, CAS registry number 50782-69-9, in pure form and in the various impure forms that may be found in military storage as well as in military industrial, depot, or laboratory operations. Agent VX is a nerve agent.

AIHC: American Industrial Health Council

AT_c: Averaging time used in HBESL calculations for carcinogens

AT_n: Averaging time used in HBESL calculations for noncarcinogens; residential, industrial

Blister Agent: A compound (such as sulfur mustard) that produces local irritation and damage to the skin, eyes and respiratory tract, and mucous membranes; injury may progress in severity to fluid-filled blisters (vesicles) on skin, depending on degree of exposure to liquid or vapor.

BW_a: Body weight for adult

BW_c: Body weight for child

BWt: Body weight for adolescent trespasser

Carcinogen: A substance or condition known to induce neoplastic change (malignancies) in experimental animals and/or man. Four types of response are generally accepted as evidence of neoplasm induction or increased carcinogenic risk:

a. An increase in incidence of the tumor types that occur vs those found in controls.

b. The development of tumors earlier than controls.

c. The occurrence of tumor types not observed in controls.

d. An increased multiplicity of tumors.

Carcinogenicity: Refers to the potential for development of cancer in a living individual. A cancer is a malignant tumor resulting from a change in the normal growth and development of cells. Cancer tumors have the tendency to invade surrounding tissue and spread to other sites in the body.

CAS: Chemical Abstracts Service

CDC: Centers for Disease Control and Prevention, U.S. Department of Health and Human Services, Atlanta, GA

CERCLA: The Comprehensive Environmental Response, Compensation, and Liability Act of 1980; also known as "Superfund".

ChE: abbreviation for cholinesterase; see definition for "cholinesterase" below.

Chemical of Potential Concern (COPC): Chemicals that are potentially site-related and whose data are of sufficient quality for use in the quantitative risk assessment.

Chemical Warfare Agent: A chemical substance intended for use in military operations to kill, seriously injure, or incapacitate people through its physiological effects. Included are blood, nerve, choking, blister, and incapacitating agents. Excluded are riot control agents, chemical herbicides, and smoke and flame materials.

Choline: One of the products from the hydrolysis of acetylcholine; $C_5H_{15}O_2N$.

Cholinesterase (ChE): A naturally occurring enzyme that catalyzes the hydrolysis of the naturally occurring neurotransmitter acetylcholine to choline (a vitamin) and an anion. Acetylcholinesterase is such an enzyme.

Chronic Reference Dose (RfD): An estimate (with uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level (usually in units of mg of chemical /kg body weight/day) for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Chronic RfDs are specifically developed to be protective for long-term exposure to a compound (as a Superfund program guideline, seven years to lifetime).

CSEPP: Chemical Stockpile Emergency Preparedness Program

COT: National Research Council Committee On Toxicology

CSF: Cancer Slope Factor; see definition for Slope Factor

Ct: concentration (often in mg/m^3) multiplied by the time period (usually in min) of exposure duration; a measure of cumulative exposure. For nerve agents, acute Cts appear to be valid only for short (approx. 10 min) periods; thus, Ct does not equal k for exposure periods greater than approx. 30-50 min. For example, a 2-minute exposure to a concentration of 100 mg/m3 [Ct = 200 mg-min/m^3 (milligram-minutes per cubic meter)], does NOT necessarily produce the same toxicological effects as a 50-minute exposure to a concentration of 4 mg/m3 (Ct = 200 mg-min/m^3) .

CVA: 2-Chlorovinyl arsonic acid

Dermal Exposure: Exposure to or by absorption through the skin.

DHHS: U.S. Department of Health and Human Services

Detection Limit (DL): The lowest amount of a compound of interest that can be distinguished from the normal "noise" of an analytical instrument or method; has been defined as 3.3 times the standard deviation of the response and slope of the calibration curve (see Krull and Swartz 1998)

Developmental Reference Dose (RfD_d): an estimate (with uncertainty spanning perhaps an order of magnitude or greater) of an exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of developmental effects. Developmental RfDs are used to evaluate the effects of a single exposure event.

DAF: Dilution Attenuation Factor

Dosage: The amount of substance administered (or received) per unit body weight or surface area (as mg/kg or mg/cm2).

Dose: The amount of agent or energy that is absorbed by the body; the amount of substance, radiation, or energy absorbed in a unit volume, an organ, or an individual (as mg/animal).

EA2192: S-(Diisopropylaminoethyl) methylphosphonothioate; a VX degradation product

Ed_c: Exposure duration for child in residential scenario (for soil contamination)

ED_i: Exposure duration for industrial scenario

ED_r: Exposure duration for residential scenario (for water contaminants)

ED_t: Exposure duration for adolescent trespasser

EF_i: Exposure frequency for industrial scenario

EF_r: Exposure frequency for residential scenario

ERAP: Environmental Risk Assessment Program; part of the Strategic Environmental Research Development Program.

Exposure: Contact of an organism with a chemical or physical agent. Exposure is quantified as the amount of the agent available at the exchange boundaries of the organism (e.g., skin, lungs, gut) and available for absorption.

Exposure Assessment: The determination or estimation (qualitative or quantitative) of the magnitude, frequency, duration, and route of exposure.

Exposure event: An incident of contact with a chemical or physical agent. An exposure event can be defined by time (e.g., day, hour) or by the incident (e.g., eating a single meal of contaminated fish).

Exposure Pathway: The course a chemical or physical agent takes from a source to an exposed organism. An exposure pathway describes a unique mechanism by which an individual or population is exposed to chemicals or physical agents at or originating from a site. Each exposure pathway includes a source or release from a source, an exposure, an exposure point, and an exposure

route. If the exposure point differs from the source, a transport/exposure medium (e.g. air) or media (in case of inter-media transfer) also is included.

FUDS: Formerly Used Defense Site

H: Henry's Law Constant; the ratio of a chemical's volatility to its water solubility. Another and separate definition is Levinstein mustard, or agent H.

HD: Distilled Mustard – see Agent HD

HBESL: Health-Based Environmental Screening Level

HEAST: Superfund Health Effects Assessment Summary Tables

Hydrolyzed: Refers to a compound which has undergone chemical reaction with liquid water or water vapor; hydrolysis is the reaction of a particular compound (such as a chemical warfare agent) with water to form new chemical compounds ("reaction products") which are degradation products of the parent compound.

IDLH: Immediately Dangerous to Life or Health; a concept originally developed by the National Institute for Occupational Safety and Health (NIOSH) in the 1970s for use in selecting respiratory protection; the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any irreversible health effects or escape-impairing effects. IDLH values are not intended for establishing permissible exposure limits. IDLH values for industrial compounds are published annually in the NIOSH *Pocket Guide to Chemical Hazards*.

IFA_{adj}: Inhalation factor, age adjusted

IFS_{adj}: Soil ingestion factor, age adjusted

$InhF_{adj}$: Inhalation factor, age adjusted

Intake: A measure of exposure expressed as the mass of a substance in contact with the exchange boundary per unit body weight per unit time (e.g., mg chemical/kg-day). Also termed the normalized exposure rate; equivalent to administered dose.

IRA_a: Inhalation rate for adult

IRA_c: Inhalation rate for child

IRA_i: Inhalation rate for industrial scenario

IRIS: The USEPA Integrated Risk Information System; a USEPA database containing verified RfDs, slope factors and up-to-date health risk and USEPA regulatory information for numerous chemicals. IRIS is USEPA's preferred source for Superfund toxicity information.

IRS_a: Soil ingestion for adult, residential scenario

IRS_c: Soil ingestion for child

IRS_i: Soil ingestion for adult, industrial scenario

Lowest-Effect Level (LEL): The lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of effects between the exposed population and its appropriate control group. Not necessarily an **adverse** effect level.

Lowest-Observed Adverse Effect Level (LOAEL): In dose-response experiments, the lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.

MCL: Maximum Contaminant Level

MCLG: Maximum Contaminant Level Guideline

MEL: Minimum Effect Level for acute toxicity; lowest exposure level at which there is detectable response.

Mustard: usually, sulfur mustard agent; the chemical bis(2-chloroethyl) sulfide, CAS registry number 505-60-2, in pure form and in the various impure formulations that may be found in chemical munitions as well as CW field, industrial, or laboratory operations; a vesicant agent. These formulations include Levinstein mustard (H), distilled mustard (HD), and closely related preparations. This definition does not apply to nitrogen mustards.

NAPL: Non Aquious-Phase Liquid

National Contingency Plan (NCP): The "National Oil and Hazardous Substances Pollution Contingency Plan" prepared by the USEPA to implement comprehensive environmental response, compensation and liability under CERCLA and the Clean Water Act; directs responsibility and procedures for cleanup of hazardous material spills. The regulations are codified at 40 CFR 300, et seq.

Nerve Agent: One of the several organic esters of phosphoric acid used as chemical warfare nerve agents because of their extreme toxicity (Tabun, GA: Sarin, GB: Soman, GD; GF, and VX). All are potent inhibitors of the enzyme, acetylcholinesterase, which is responsible for the degradation of the neurotransmitter, acetylcholine. Symptoms result from excess accumulation of acetylcholine in neuronal synapses or myoneural junctions. Nerve agents are readily absorbed by inhalation and/or through intact skin.

NIOSH: The National Institute for Occupational Safety and Health of the U.S. Department of Health and Human Services

NRC: the National Research Council

Non-detects (NDs): Chemicals that are not detected in a particular sample at concentrations below a certain limit, usually the detection limit for the chemical in that sample. Non-detects may be indicated by a "U" data qualifier.

No-Observed Adverse Effects Level (NOAEL): In dose-response experiments, an exposure level at which there are no statistically or biologically significant increases in the frequency or severity of

adverse effects (to tissue, cells, organs, etc.) between the exposed population and its appropriate control (some effects may be produced at this level, but they are not considered as adverse, nor precursors to specific adverse effects). The NOAEL is the highest exposure level without adverse effect.

No-Observed Effects Level (NOEL): An exposure level at which there are no statistically or biologically significant increases in the frequency or severity of any effect (to tissue, cells, organs, etc.) between the exposed population and its appropriate control.

ORNL: Oak Ridge National Laboratories

OSHA: Occupational Safety and Health Administration

OSWER: USEPA Office of Solid Waste and Emergency Response

OTSG: Office of The (Army) Surgeon General

PEF: Particulate Emission Factor

Percutaneous Exposure: The absorption of a contaminant through the unbroken skin.

PPE: Personal Protective Equipment

ppm: Parts per million

PRG: USEPA Region IX Preliminary Remediation Goal model (see USEPA 1996a)

Quantitation Limit (QL): The lowest level at which a chemical can be accurately and reproducibly detected. Variously defined; one recent definition is 10 times the standard deviation of the response and slope of the calibration curve (Krull and Swartz, 1998); definition varies for different chemicals and different samples.

RAGS: Risk Assessment Guidance for Superfund; the document *Risk Assessment Guidance for Superfund, volume 1: Human Health Evaluation Manual,* Parts A and B. EPA/540/1-89/002 and Pub. # 9285.7-01B of the USEPA Office of Emergency Response (1989).

RASH: Rapid Screening of Hazard relative potency approach for the assessment of toxicity; documented in Jones et al 1985 and Jones et al 1988

Reference Concentration (RfC): An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime.

Reference Dose (RfD): the USEPA's preferred toxicity value (in units of mg chemical/kg body weight/day) for evaluating noncarcinogenic effects resulting from exposure at Superfund sites. See specific entries for chronic RfD, subchronic RfD, and developmental RfD. The acronym RfD, when used without other modifiers, either refers generically to all types of RfDs or specifically to chronic RfDs; it never refers specifically to subchronic or developmental RfDs.

Remedial Actions: Actions taken to restore a contaminated site to its pre-contaminated condition. In contrast to removal actions, these are longer-term actions, including cleanup, treatment, and neutralization of contamination and access control or permanent relocation of residents, if necessary. Remedial actions are coordinated by the remedial project manager. U.S. Department of the Army Pamphlet (DA PAM) 50-6, *Chemical Accident or Incident Response and Assistance (CAIRA) Operations*, treats remedial actions as taking place in a "non-emergency atmosphere," and describes the goal as returning the chemical accident or incident site to "technically achievable and acceptable conditions."

RBC: USEPA Region III Risk-Based Concentration model

RME: Reasonable maximum exposure; the highest exposure that is reasonably expected to occur at a site

SA_a: Exposed skin surface for adult

SA_c: Exposed skin surface for child

Sarin: Isopropyl methylphosphonofluoridate, CAS number 107-44-8; it is a nonpersistent organophosphate nerve agent also known as Agent GB. Its chemical formula is C4H10FO2P.

SERDP: Strategic Environmental Research Development Program

SFS_{adj}: Soil contact factor, age adjusted

Slope Factor: A plausible upper-bound estimate of the probability of a response per unit intake of a chemical over a lifetime. The slope factor is used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a potential carcinogen.

Soman: Pinacolyl methyl phosphonofluoridate, CAS number 96-64-0; nerve agent GD. Its chemical formula is $(CH_3)_3CCH(CH_3)OPF(O)CH_3$.

SSL: USEPA-OSWER Soil Screening Level model

STEL: Short-Term Exposure Limit; see also definition for TLV-STEL

Subchronic reference dose (RfD_s): An estimate (with uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a portion of a lifetime (as a Superfund program guideline, two weeks to seven years).

Sulfur Mustard: A blister agent also known as Agent H (or HD for distilled mustard); bis(2-chloroethyl) sulfide, CAS number 505-60-2. The chemical formula is $C_4H_8Cl_2S$.

Tabun: Ethyl N,N-dimethylphosphoramidocyanidate, CAS number 77-81-6. A non-persistent organophosphate nerve agent also known as Agent GA. Its chemical formula is $C_5H_{11}N_2O_2P$.

Threshold Limit Value (TLV®): TLV® is a registered trademark of the American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio. A value that refers to airborne concentrations of substances and represents conditions under which it is believed nearly all

workers may be repeatedly exposed day after day, without adverse health effects. A table of these values and accompanying precautions is published annually by the ACGIH. Use of trademarked name does not imply endorsement by the U.S. Army but is intended only to assist in identification of a specific product.

Threshold Limit Value Categories:

a. Threshold Limit Value-Time-Weighted Average (TLV-TWA). The time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

b. Threshold Limit Value-Short-Term Exposure Limit (TLV-STEL). The concentration to which workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue, or materially reduce work efficiency, provided that the daily TLV-TWA is not exceeded. The STEL is not a separate independent exposure limit; rather, it supplements the time-weighted average (TWA) limit where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. Exposures up to the STEL should not be longer than 15 minutes and should not occur more than four times per day, with a period of at least 60 min between successive exposures.

c. Threshold Limit Value--Ceiling (TLV-C). The concentration that should not be exceeded during any part of the working exposure.

Time-Weighted Average (TWA) Concentration: The concentration of airborne material that has been weighted for the time duration, usually eight hours. A sufficient number of samples are needed to determine a TWA concentration throughout a complete cycle of operations or through the work shift.

Time-Weighted Average Exposure: An average over a given (working) period of an individual's exposure, as determined by sampling at given times during the period.

Toxicity: The capacity of a chemical to act as a poison in producing harmful effects on living organisms; the nature, degree, and extent of undesirable effects.

TR: target excess individual lifetime cancer risk (unitless)

Uncertainty Factor (UF): One of several adjustment factors used in operationally deriving a RfD from experimental data and representing a specific area of uncertainty inherent in the extrapolation from available data. Each UF value is often 10, although values <10 can also be used. UFs are intended to account for:

a. Human to sensitive human; intended to protect sensitive subpopulations.

b. Animal to human; extrapolating from animal data to the case of humans.

c. Subchronic to chronic; extrapolating from a subchronic study to derive a chronic RfD.

d. LOAEL to NOAEL; when a suitable NOAEL is not available and a LOAEL is used instead.

e. Incomplete to complete database; when available data do not adequately address all possible adverse outcomes in humans.

USACHPPM: U.S. Army Center for Health Promotion and Preventive Medicine

USEPA: U.S. Environmental Protection Agency

Vesicant: Causing blisters or vesicles. Sulfur mustard agent (HD) and Lewisite (L) are both vesicant agents.

VF_s: Volatilization Factor for soil

VF_w: Volatilization Factor for tapwater.

VLEACH: a one-dimensional finite difference vadose zone leaching model. The model estimates the impact on underlying ground water of the mobilization and migration of sorbed organic pollutants located in the vadose zone.

REFERENCES

DA (Departmant of the Army). 1994. *Glossary of Terms for Chemical Agents and Chemical defense Equipment.* TG 204. Headquarters, Department of the Army, Washington, DC.

Jones, TD, PJ Walls and EA Zeighami, 1985. "Permissible concentrations of chemicals in air and water derived from RTECS entries; a 'RASH' chemical scoring system. " *J. Toxicol. Ind. Health* 1:213-234

Jones TD, PJ Walsh, AP Watson, BA Owen, LW Barnthouse, DW Sanders, 1988. "Chemical scoring by a Rapid Screening Hazard (RASH) method." *Risk Anal.* 8:99-118

Krull, I., and M. Swartz, 1998. "Determining limits of detection and quantitation," LC-GC, 16 (10): 822-824

USEPA, 1996a. *EPA Region IX Preliminary Remediation Goals (PRGs)*, August 1, 1996. EPA Contact: Standford J. Smucker, EPA Region IX, San Francisco, CA.

USEPA, 1996b. *EPA Region III Risk-Based Concentration Table, Background Information. Development of Risk-Based Concentrations*. April 30, 1996. EPA Contact: Roy L. Smith, EPA Region III, Office of Superfund Programs, Philadelphia, PA. (Online file at http://www.epa.gov/reg3hwmd/risk/guide4.htm; retrieved March 31, 1997).

APPENDIX A

DERIVATION OF CHEMICAL PARAMETERS

A.1 HENRY'S LAW CONSTANT

This constant is a ratio of the volatility of a chemical to its water solubility, and thus is a measure of the tendency of a chemical to volatilize from water. Henry's Law Constants can be determined experimentally or estimated from the vapor pressure and water solubility of the chemical.

$$H = \frac{V}{S} \qquad \text{(A-1)}$$

where:
V = vapor pressure (in atm)
S = water solubility (in mol/m^3)

or

$$H = H^* \times R \times T \qquad \text{(A-2)}$$

where:
H* = ratio of the volatility (in mg/m^3) and water solubility (in mg/m^3)
R = gas constant (8.2 x 10^{-5} atm·m^3/mol·K)
T = temperature in K (20°C = 293.15°K)

Henry's Law Constants for the chemical warfare agents were derived using both Equation A-1 and Equation A-2. The derived values are presented in Table A-1.

A.2 DIFFUSION COEFFICIENTS

A.2.1 Diffusivity in Air

For the diffusion of a chemical in air the following formula is recommended (USEPA, 1994a):

$$Di = 0.0067T^{1.5} (0.034 + M^{-1})^{0.5} M^{-0.17} [(M/2.5d)^{0.33} + 1.81]^{-2} \qquad \text{(A-3)}$$

where:

T	=	Absolute temperature (degrees Kelvin)
M	=	Molecular weight (g/g mol)
d	=	Density of liquid chemical (g/cm^3)

Table A-1. Vapor pressure, Solubility and Henry's Law Constants for Chemical Warfare Agents									
Chemical (mol. wt)	Vapor pressure (mm Hg)	Vapor Pressure (atm)	Volatility (mg/m^3)	Solubility (g/100 g)	Solubility (mg/m^3)	Solubility (mol/m^3)	Henry's Law Constant ($atm \cdot m^3/mol$)		
							Derived from Equation A-1	Derived from Equation A-2	Literature Value[a]
HD[b] (159.08)	0.11[c]	1.4×10^{-4}	920[c]	0.092[d]	9.2×10^{5}	5.8[c]	2.4×10^{-5}	2.4×10^{-5}	2.1×10^{-5}
Lewisite (207.32)	0.58[c]	7.6×10^{-4}	6500[c]	0.05[f,g]	5×10^{5}	2.4	NA[g]	NA[g]	-
GA (162.1)	0.07[c]	9.2×10^{-5}	610[c]	9.8[c]	9.8×10^{7}	604.6	1.5×10^{-7}	1.5×10^{-7}	-
GB (140.1)	2.9[c]	3.8×10^{-3}	22000[c]	miscible	miscible	miscible	-	-	5.4×10^{-7}
GD (182.2)	0.40[c]	5×10^{-4}	3900[c]	2.1[c]	2.1×10^{7}	115.3	4.3×10^{-6}	4.5×10^{-6}	-
VX (267.4)	0.0007[c]	9×10^{-7}	10.5[c]	3[c]	3×10^{7}	112.2	8.0×10^{-9}	8.4×10^{-9}	3.5×10^{-9}

Source: Vapor pressure, volatility, and solubility data from DA, 1974

[a] Small, 1984

[b] Volatility and solubility data not for same temperature.

[c] At 25°C

[d] At 22°C

[e] At 20°C

[f] MacNaughton and Brewer, 1994

[g] Lewisite hydrolyzes so rapidly that measurements of solubility and calculation of H are not meaningful (Rosenblatt et al., 1975)

A.2.1.1 Sulfur Mustard. The molecular weight of HD is 159.02 and the liquid density is 1.27 g/ml. At a temperature of 300°K, the air diffusivity coefficient for HD is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 159.02^{-1})^{0.5} 159.02^{-0.17} [(159.02/(2.5 \times 1.27))^{0.33} + 1.81]^{-2} \quad \text{(A-4)}$$

$$Di = 0.099$$

A.2.1.2 Lewisite. The molecular weight of Lewisite is 207.32 and the liquid density is 1.88 g/ml. At a temperature of 300°K, the air diffusivity coefficient for Lewisite is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 207.32^{-1})^{0.5} 207.32^{-0.17} [(207.32/(2.5 \times 1.88))^{0.33} + 1.81]^{-2} \quad \text{(A-5)}$$

$$Di = 0.099$$

A.2.1.4 Agent GA. The molecular weight of GA is 162.1 and the liquid density is 1.09 g/ml. At a temperature of 300°K, the air diffusivity coefficient for GA is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 162.1^{-1})^{0.5} 162.1^{-0.17} [(162.1/(2.5 \times 1.09))^{0.33} + 1.81]^{-2} \quad \text{(A-6)}$$

$$Di = 0.092$$

A.2.1.3 Agent GB. The molecular weight of GB is 140.1 and the liquid density is 1.09 g/ml. At a temperature of 300°K, the air diffusivity coefficient for GB is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 140.1^{-1})^{0.5} 140.1^{-0.17} [(140.1/(2.5 \times 1.09))^{0.33} + 1.81]^{-2} \quad \text{(A-7)}$$

$$Di = 0.101$$

A.2.1.5 Agent GD. The molecular weight of GD is 182.2 and the liquid density is 1.02 g/ml. At a temperature of 300°K, the air diffusivity coefficient for GD is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 182.2^{-1})^{0.5} 182.2^{-0.17} [(182.2/(2.5 \times 1.02))^{0.33} + 1.81]^{-2} \quad \text{(A-8)}$$

$$Di = 0.082$$

A.2.1.6 Agent VX. The molecular weight of VX is 267.37 and the liquid density is 1.0083 g/mL. At a temperature of 300°K, the air diffusivity coefficient for VX is:

$$Di = 0.0067 \times 300^{1.5} (0.034 + 267.37^{-1})^{0.5} 267.37^{-0.17} [(267.37/(2.5 \times 1.0083))^{0.33} + 1.81]^{-2} \quad \text{(A-9)}$$

$$Di = 0.062$$

A.2.2 Diffusivity in Water

For the diffusion of a chemical in water the following formula is recommended (USEPA, 1994a):

$$D_w = 1.518 (10^{-4}) V_{cm}^{-0.6} \quad \text{(A-10)}$$

where:

D_w	=	Diffusion coefficient in water
V_{cm}	=	Molar volume (M/d)
M	=	Molecular weight of chemical
d	=	Density of liquid chemical at room temperature (g/cm^3)

therefore:

$$D_w = 1.518 (10^{-4}) (M/d)^{-0.6} \quad \text{(A-11)}$$

A.2.2.1 Sulfur Mustard. The molecular weight of HD is 159.02 and the liquid density is 1.27 g/cm^3. At room temperature, the water diffusivity coefficient for sulfur mustard is:

$$D_w = 1.518 (10^{-4}) (159.02/1.27)^{-0.6} \quad \text{(A-12)}$$

A.2.2.2 Lewisite. The molecular weight of Lewisite is 207.32 and the liquid density is 1.88 g/ml. At room temperature, the water diffusivity coefficient for Lewisite is:

$$D_w = 1.518 (10^{-4}) (207.32/1.88)^{-0.6} \quad \text{(A-13)}$$

A.2.2.3 Agent GA. The molecular weight of GA is 162.1 and the liquid density is 1.09 g/ml. At room temperature, the water diffusivity coefficient for agent GA is:

$$D_w = 1.518\ (10^{-4})\ (162.1/1.09)^{-0.6} \quad \text{(A-14)}$$

A.2.2.4 Agent GB. The molecular weight of GB is 140.1 and the liquid density is 1.09 g/ml. At room temperature, the water diffusivity coefficient for agent GB is:

$$D_w = 1.518\ (10^{-4})\ (140.1/1.09)^{-0.6} \quad \text{(A-15)}$$

A.2.2.5 Agent GD. The molecular weight of GD is 182.2 and the liquid density is 1.02 g/ml. At room temperature, the water diffusivity coefficient for agent GD is:

$$D_w = 1.518\ (10^{-4})\ (182.2/1.02)^{-0.6} \quad \text{(A-16)}$$

A.2.2.6 Agent VX. The molecular weight of VX is 267.37 and the liquid density is 1.0083 g/ml. At room temperature, the water diffusivity coefficient for agent VX is:

$$D_w = 1.518\ (10^{-4})\ (267.37/1.0083)^{-0.6} \quad \text{(A-17)}$$

A.2.3 Apparent Diffusivity. The equation for deriving the apparent diffusivity (D_A) of a chemical is as follows:

$$D_A = \frac{[(\Theta_a^{10/3} D_i H' + \Theta_w^{10/3} D_w)/n^2]}{\rho_b K_d + \Theta_w + \Theta_a H'} \quad \text{(A-18)}$$

where (default values are given in parentheses):

D_A = Apparent diffusivity (cm^2/s)
Θ_a = Air-filled soil porosity (0.28 L_{air}/L_{soil}, or n-Θ_w)
D_i = Diffusivity in air (cm^2/sec), chemical specific (see below)
H' = Dimensionless Henry's Law Constant, chemical specific (41 x H)
Θ_w = Water-filled soil porosity (0.15 L_{water}/L_{soil})
D_w = Diffusivity in water (cm^2/sec), chemical specific (see below)
n = Total soil porosity (0.43 L_{air}/L_{soil}, or 1-(ρ_b/ρ_s)

ρ_b = Dry soil bulk density (1.5 g/cm^3)
K_d = Soil-water partition coefficient (cm^3/g) = K_{oc} x f_{oc})
K_{oc} = Soil-organic carbon partition coefficient (chemical specific)
f_{oc} = Percent organic carbon in soil (EPA Region IX default, 0.006)
ρ_s = Soil particle density (2.65 g/cm^3)

A.2.3.1 Sulfur Mustard. The chemical-specific parameters for sulfur mustard are: $D_i = 0.099$, $H' = 8.61 \times 10^{-4}$, $D_w = 8.4 \times 10^{-6}$, and $K_d = 0.798$.

$$D_A = \frac{[((0.28)^{10/3} \times 0.099 \times 8.61 \times 10^{-4}) + ((0.15)^{10/3} \times 8.4 \times 10^{-6})]/(0.43)^2}{(1.5 \times 0.798) + 0.15 + (0.28 \times 8.61 \times 10^{-6})} \quad \text{(A-19)}$$

$$D_A = 5 \times 10^{-6}$$

A.2.3.2 Lewisite. The chemical-specific parameters for Lewisite: $D_i = 0.099$, $H' = 1.31 \times 10^{-2}$, and $D_w = 9.0 \times 10^{-6}$. A K_d cannot be estimated from a K_{ow} because the latter is not available due to rapid hydrolysis of the agent; therefore, the apparent diffusivity of Lewisite cannot be calculated.

A.2.3.3 Agent GA. The chemical-specific parameters for agent GA are: $D_i = 0.092$, $H' = 6.15 \times 10^{-6}$, $D_w = 7.5 \times 10^{-6}$, and $K_d = 0.231$.

$$D_A = \frac{[((0.28)^{10/3} \times 0.092 \times 6.15 \times 10^{-6}) + ((0.15)^{10/3} \times 7.5 \times 10^{-6})]/(0.43)^2}{(1.5 \times 0.231) + 0.15 + (0.28 \times 6.15 \times 10^{-6})} \quad \text{(A-20)}$$

$$D_A = 2.35 \times 10^{-7}$$

A.2.3.4 Agent GB. The chemical-specific parameters for agent GB are: $D_i = 0.10$, $H' = 2.2 \times 10^{-5}$, $D_w = 8.2 \times 10^{-6}$, and $K_d = 0.208$.

$$D_A = \frac{[((0.28)^{10/3} \times 0.10 \times 2.2 \times 10^{-5}) + ((0.15)^{10/3} \times 8.2 \times 10^{-6})]/(0.43)^2}{(1.5 \times 0.208) + 0.15 + (0.28 \times 2.2 \times 10^{-5})} \quad \text{(A-21)}$$

$$D_A = 5.4 \times 10^{-7}$$

A.2.3.5 Agent GD. The chemical-specific parameters for agent GD are: $D_i = 0.082$, $H' = 1.87 \times 10^{-4}$, $D_w = 6.8 \times 10^{-6}$, and $K_d = 1.404$.

$$D_A = \frac{[((0.28)^{10/3} \times 0.082 \times 1.87 \times 10^{-4}) + ((0.15)^{10/3} \times 6.8 \times 10^{-6})]/(0.43)^2}{(1.5 \times 1.404) + 0.15 + (0.28 \times 1.87 \times 10^{-4})} \quad \text{(A-22)}$$

$$D_A = 5.57 \times 10^{-7}$$

A.2.3.6 Agent VX. The chemical-specific parameters for agent VX are: $D_i = 0.062$, $H' = 1.435 \times 10^{-7}$, $D_w = 5.3 \times 10^{-6}$, and $K_d = 1.962$.

$$D_A = \frac{[((0.28)^{10/3} \times 0.062 \times 1.43 \times 10^{-7}) + ((0.15)^{10/3} \times 5.3 \times 10^{-6})/(0.43)^2]}{(1.5 \times 1.962) + 0.15 + (0.28 \times 1.43 \times 10^{-7})} \quad \text{(A-23)}$$

$$D_A = 1.68 \times 10^{-8}$$

A.3 VOLATILIZATION FACTOR FOR SOIL (VF_s)

The equation for deriving the volatilization factor for soil (VF_s) of a chemical is as follows:

$$VF_S = (\frac{Q}{C}) \times \frac{(3.14 \times D_A \times T)^{1/2}}{2 \times \rho_b \times D_A} \times 10^{-4}\ m^2/cm^2 \quad \text{(A-24)}$$

where (default values are given in parentheses):

VF_s	=	Volatilization Factor (m^3/kg)
D_A	=	Apparent diffusivity (cm^2/s)
Q/C	=	Inverse of the mean concentration at the center of a 0.5 acre square source (68.81 $g/m^2 \cdot s$ per kg/m^3).
T	=	Exposure interval (9.5×10^8 sec)
ρ_b	=	Dry soil bulk density ($1.5\ g/cm^3$)

A.3.1 Sulfur Mustard. The apparent diffusivity of HD is 5×10^{-6} cm^2/s.

$$VF_S = 68.81 \times \frac{(3.14 \times 5 \times 10^{-6} \times 9.5 \times 10^8)^{1/2}}{2 \times 1.5 \times 5 \times 10^{-6}} \times 10^{-4} \quad \text{(A-25)}$$

$$VF_S = 5.6 \times 10^4$$

A.3.2 Agent GB. The apparent diffusivity (D_A) of agent GB is 5.4×10^{-7} cm^2/s.

$$VF_S = 68.81 \times \frac{(3.14 \times 5.4 \times 10^{-7} \times 9.5 \times 10^{8})^{1/2}}{2 \times 1.5 \times 5.4 \times 10^{-7}} \times 10^{-4} \quad \text{(A-26)}$$

$$VF_s = 1.7 \times 10^{5}$$

A.3.3 Agent GA. The apparent diffusivity (D_A) of agent GA is 2.35 x 10^{-7} cm^2/s.

$$VF_S = 68.81 \times \frac{(3.14 \times 2.35 \times 10^{-7} \times 9.5 \times 10^{8})^{1/2}}{2 \times 1.5 \times 2.35 \times 10^{-7}} \times 10^{-4} \quad \text{(A-27)}$$

$$VF_s = 2.6 \times 10^{5}$$

A.3.4 Agent GD. The apparent diffusivity (D_A) of agent GD is 5.57 x 10^{-7} cm^2/s.

$$VF_S = 68.81 \times \frac{(3.14 \times 5.57 \times 10^{-7} \times 9.5 \times 10^{8})^{1/2}}{2 \times 1.5 \times 5.57 \times 10^{-7}} \times 10^{-4} \quad \text{(A-28)}$$

$$VF_s = 1.7 \times 10^{5}$$

A.3.5 Agent VX. The apparent diffusivity (D_A) of agent VX is 1.68 x 10^{-8} cm^2/s.

$$VF_S = 68.81 \times \frac{(3.14 \times 1.68 \times 10^{-8} \times 9.5 \times 10^{8})-}{2 \times 1.5 \times 1.68 \times 10^{-8}} \times 10^{-4} \quad \text{(A-29)}$$

$$VF_s = 9.7 \times 10^{5}$$

A.4 SOIL SATURATION LIMIT (C_{sat})

The soil saturation limit (C_{sat}) is the contaminant concentration at which soil pore air and pore water are saturated with the chemical and the adsorptive limits of the soil particles have been reached (USEPA, 1996c). Above this concentration, the contaminant exists in the soil in the free phase, and Equation 2-1 cannot be used to estimate the Volatilization Factor. VF-based screening levels are not accurate for concentrations above the C_{sat}. The C_{sat} for each chemical can be estimated as follows (USEPA, 1996c):

$$C_{sat} = \frac{S}{\rho_b} (K_d \rho_b + \Theta_w + H'\Theta_a) \quad \text{(A-30)}$$

where:

C_{sat}	=	Soil Saturation concentration (mg/kg)
S	=	Solubility in water (mg/L), chemical specific
ρ_b	=	Dry soil bulk density (1.5 kg/L)
K_d	=	Soil-water partition coefficient [$(cm^3/g) = K_{oc} \times f_{oc}$]
K_{oc}	=	Soil organic carbon-water partition coefficient (chemical-specific), used to calculate K_d
f_{oc}	=	Percent organic carbon in soil (EPA Region IX default, 0.006)
Θ_w	=	Water-filled soil porosity (0.15 L_{water}/L_{soil})
H′	=	Dimensionless Henry's Law Constant, chemical-specific (41 x Henry's Law Constant)
Θ_a	=	Air-filled soil porosity (0.28 L_{air}/L_{soil}, or n-Θ_w)
n	=	Total soil porosity [0.43 L_{air}/L_{soil}, or 1-(ρ_b/ρ_s)]
ρ_s	=	Soil particle density (2.65 g/cm^3), used to calculate n

The EPA default values are given in parentheses. Soil saturation limits for the chemical agents are listed in Table 2-3. Agent GB is miscible with water. A soil saturation limit cannot be derived for Lewisite because of the rapid hydrolysis of the compound.

A.5 PARTICULATE EMISSION FACTOR (PEF)

Inhalation of fugitive dusts is an exposure pathway that is considered in deriving Preliminary Remediation Goals and Soil Screening Levels (SSLs). Derivation of a fugitive dust SSL requires calculation of a PEF that relates the concentration of the chemical in soil to its concentration in dust particles in air. The PEF represents an annual average emission rate based on wind erosion. The PEF is calculated as follows:

$$PEF = \left(\frac{Q}{C}\right) \times \frac{3{,}600 \text{ sec/hr}}{0.036 \times (1 - V) \times (U_m/U_t) \times F(x)} \qquad \text{(A-31)}$$

where:

PEF	=	Particulate emission factor (1.32×10^9 m^3/kg)
Q/C	=	Inverse of the mean concentration at the center of a 0.5 acre square source (90.80 $g/m^2 \cdot s$ per kg/m^3)
V	=	Fraction of vegetative cover (50%)
U_m	=	Mean annual wind speed (4.69 m/s)
U_t	=	Equivalent threshold value of windspeed at 7 m (11.32 m/s)
F(x)	=	Function dependent on U_m/U_t; see Cowherd et al., 1985 (0.194)

APPENDIX B

CARCINOGENIC POTENCY FOR SULFUR MUSTARD

This Appendix contains a copy of a letter received from Dr. David Gaylor, National Center for Toxicological Research, Food and Drug Administration, Jefferson, Arkansas. Dr. Gaylor had previously made comments and shared his expertise regarding various approaches to evaluating the carcinogenic potency of chemicals. As a member of the National Research Council Committee on Toxicology (COT), Subcommittee on Chronic Reference Doses for Selected Chemical Warfare Agents, reviewing chronic toxicological data for the chemical warfare agents, he was familiar with the available toxicity data for sulfur mustard. The Army requested that Dr. Gaylor provide documentation of his own evaluation of the carcinogenic potency of sulfur mustard.

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
Food and Drug Administration

Phone: (501) 543-7000 (870) 543-7001 (Voice)
(870) 543-7576 (FAX)

National Center
For Toxicological Research
3900 NCTR Road
Jefferson AR 72079-9502

March 11, 1998

Ms. Veronique Hauschild
Hazardous and Medical Waste Program
U.S. Army Center for Health Promotion
and Preventive Medicine
Bldg. E-1675
Aberdeen Proving Ground, MD 21010-5422

Dear Ms. Hauschild:

Dr. Annetta Watson, Oak Ridge National Laboratory, asked me to share with you my analysis of the potential cancer risk from long-term, low-dose oral exposure to sulfur mustard (enclosed). As you know, this is one of the agents being evaluated by a National Research Council subcommittee. That subcommittee is still evaluating sulfur mustard and other agents. Hence, the enclosed comments are strictly my own at this time and do not necessarily represent those of the subcommittee. This material has been submitted to the subcommittee, but it could undergo substantial revision review conducted by the National Research Council.

I would be available to discuss this material further with you. I can be reached by telephone: [870] 543-7001; fax: [870] 543-7576; and e-mail: dgaylor@nctr.fda.gov.

Sincerely,

David W. Gaylor, Ph.D.
Assoc. Dir. for Risk Assessment
Policy and Research
NCTR/FDA

Enclosure

cc:
Dr. Annetta Watson, Oak Ridge National Laboratory
Dr. Kulbir Bakshi, National Research Council

Revised for Army

Carcinogenic Potency for Sulfur Mustard

D.W. Gaylor, Ph.D.

March 11, 1998

There are a number of human studies that provide estimates of the relative risk for cancer associated with exposure to sulfur mustard. The duration of exposure is reported for some of these studies, but there was no indication of the dose levels. Hence, it is not possible to estimate the carcinogenic potency (risk per mg/kg-d) from the reported human data.

There has not been a chronic study in which animals were administered sulfur mustard orally. However, there are several indirect methods for estimating the carcinogenic potency of sulfur mustard. These are summarized in the following discussion.

Watson et al. (1989) argue that the carcinogenic potency of sulfur mustard is 1.3 times that of benzo(a)pyrene. The carcinogenic potency of benzo(a)pyrene listed in the USEPA Integrated Risk Information System is less than 7.3 per mg/kg-d. Hence, the estimated carcinogenic potency for sulfur mustard is less than 1.3 x 7.3 = 9.5 per mg/kg-d by this approach.

In a recent chronic feeding study of benzo(a)pyrene conducted in B6C3F1 female mice (Culp et al., 1998), the incidence of forestomach tumors were 1/48, 3/47, 36/46, and 46/47 at 0, 5, 26, and 100 ppm, respectively. The carcinogenic potency of benzo(a)pyrene was estimated to be less then 1.2 per mg/kg-d, assuming equal potency between animals and humans for dose adjusted by body weight to the 3/4 power. Note that this is 1/6 of the current USEPA potency value for benzo(a)pyrene. If sulfur mustard is 1.3 times more potent than benzo(a)pyrene (Watson et al., 1989), the carcinogenic potency for sulfur mustard is estimated to be less than 1.3 x 1.2 = 1.6 per mg/kg-d based on the carcinogenicity of benzo(a)pyrene observed by Culp et al. (in press).

Sasser et al. (1989a) observed forestomach hyperplasia in male and female Sprague-Dawley rats gavaged with sulfur mustard in sesame oil, 5 days per week for 13 weeks. The incidence of hyperplasia was 0/24, 0/24, 0/24, 0/24, 1/24, and 10/24 at 0, 0.003, 0.01, 0.03, 0.1, and 0.3 mg/kg-d, respectively. Making the conservative assumption that hyperplasia at 13 weeks may serve as a biomarker for potential tumorigenicity, the multistage model was fit to these data providing an estimate of 10% incidence at 0.16 mg/kg-d. The lower 95% confidence limit on this dose was 0.10 mg/kg-d. Adjusting this dose for gavaging on 5 days per week and body weight to the 3/4 power results in a lower confidence limit of 0.02 mg/kg-d. In accordance with the proposed carcinogen risk assessment guidelines (USEPA, 1996), linear extrapolation to zero gives a potential carcinogenic potency of less than 0.1/0.02 = 5.0 per mg/kg-d.

Sasser et al. (1989b) observed benign forestomach lesions in male and female Sprague-Dawley rats gavaged in a two-generation reproductive study with sulfur mustard. The incidence of lesions was 0/94, 0/94, 8/94, and 10/94 at 0. 0.3, 0.1, and 0.4 mg/kg-d. Making the conservative assumption that these lesions may serve as a biomarker for potential tumorigenicity, the multistage model was fit to these data providing a 10% incidence at 0.28 mg/kg-d, with a lower 95% confidence limit of 0.19 mg/kg-d. Adjusting this dose for gavage on 5 days per week and body weight to the 3/4 power results in a lower

confidence limit of 0.038 mg/kg-d. Following the proposed carcinogen risk assessment guidelines (USEPA, 1996), linear extrapolation to zero gives a potential carcinogenic potency of less then 0.1/0.038 = 2.6 per mg/kg-d of sulfur mustard.

Gaylor and Gold (1995) observed for 139 animal carcinogens tested in the National Toxicology Program that carcinogenic potency can be estimated by 0.74 divided by the maximum tolerated dose, expressed in terms of mg/kg-d. Sasser et al. (1989a) reported significant body weight depression in rats administered 0.3 mg/kg-d sulfur mustard for 90 days. No toxic effects were noted at 0.1 mg/kg-d. Hence, a dose of 0.2 mg/kg-d might serve as the maximum dose in a 2-year study. With a maximum tolerated dose of 0.2 mg/kg-d for 5 days per week, the average daily dose at the maximum tolerated dose of 0.2 x (5/7) = 0.14 mg/kg-d. From Gaylor and Gold (1995), an estimate of the carcinogenic potency is less than 0.74/0.14 = 5.3 per mg/kg-d of sulfur mustard.

In the absence of a chronic bioassay for sulfur mustard, these diverse methods for estimating an upper limit on the carcinogenic potency gave remarkably similar results of 1.6 to 9.5 per mg/kg-d for lifetime exposure (Table B). I would expect a 2-year rodent bioassay to yield results in or near this range. Cancer risk is estimated to be less than the carcinogenicity potency times the average lifetime daily dose. For example, if it were desired to restrict the potential carcinogenic risk from ingestion of sulfur mustard to less than 10^{-5} for those individuals exposed for a lifetime, daily oral doses should probably be limited to $10^{-5}/1.6 = 6 \times 10^{-6}$ mg/kg-d to $10^{-5}/9.5 = 1 \times 10^{-6}$ mg/kg-d. This is about the same range of doses derived for the reference dose for noncancer effects.

Table B-1. Estimates of the upper limit for carcinogenic potency (risk per mg/kg-d) of sulfur mustard

Method of Estimation	Estimate
Potency relative to benzo(a)pyrene potency from the USEPA IRIS (Watson et al., 1989)	9.5
Potency relative to benzo(a)pyrene potency from Culp at al. (1998)	1.6
Linear extrapolation from the benchmark dose of forestomach hyperplasia (Sasser et al., 1989a)	5.0
Linear extrapolation from the benchmark dose of forestomach lesions (Sasser et al., 1989b)	2.6
Relative to the maximum tolerated dose (Gaylor and Gold, 1995)	5.3

REFERENCES

Culp, S.J., Gaylor, D.W., Sheldon, W.G., Goldstein, L.S., and Boland, F.A. in press. A comparison of the tumors induced by coal tar and benzo[a]pyrene in a two year bioassay. *Carcinogenesis*.

Gaylor, D.W. and Gold, L.S. 1995. Quick estimate of the regulatory virtually safe dose based on the maximum tolerated dose for rodent bioassays. *Regulatory Toxicol. Pharmacol.* **22**:57-63.

Sasser, L.B., Miller, R.A., Kalkwarf, D.R., et al. 1989a. *Toxicology Studies on Lewisite, and Sulfur Mustard Agents: Subchronic Toxicity of Sulfur Mustard (HD) in Rats.* Final Report, PNL-6870. Pacific Northwest Laboratory, Richland, Washington.

Sasser, L.B., Miller, R.A., Kalkwarf, D.R., Buschbom, R.L., and Cushing J.A. 1989b. *Toxicology Studies on Lewisite and Sulfur Mustard Agents: Two-Generation Reproduction Study of Sulfur Mustard (HD) in Rats.* Final Report, PNL-6944. Pacific Northwest Laboratory, Richland, Washington.

U.S. Environmental Protection Agency (USEPA). 1996. Proposed guidelines for carcinogen risk assessment: Notice, *Federal Register* **61** (79):17960-18011.

Watson, A.P., Jones, T.D., and Griffin, G.D. 1989. Sulfur mustard as a carcinogen: application of relative potency analysis to the chemical warfare agents H, HD, and HT. *Regulatory Toxicol. Pharmacol.* **10**:1-25.

APPENDIX C

SCREENING VALUES FOR TRESPASSERS

C.1 OBJECTIVE

The objective of this section is to provide an example of how the Preliminary Remediation Goal (PRG) and Risk Based Concentration (RBC) models can be used to evaluate potential chronic health risks to trespassers from exposures to soil containing residual chemical warfare agents sulfur mustard (HD) and Lewisite, and the nerve agents Tabun (GA), Sarin (GB), Soman (GD), and VX.

The example provided is a theoretically-based scenario which uses assumptions that are intended to be reasonably conservative. However, parameter values used in the trespasser scenario are highly variable in real-world situations. Therefore, site-specific risk assessment in these scenarios is advised. The values chosen for these examples, though intended to be conservative, may not be sufficiently conservative for all situations, while in other circumstances, the application of the risk assessment model itself may not be appropriate. For example, if conditions exist such that trespasser exposures may be as high as 50 days each year, then the values used in these examples (12 days each year) would not be conservative enough. On the other hand, other real-world exposure scenarios may not present a chronic/repeated exposure problem (i.e., if trespassers do not regularly and repeatedly come in contact with soil containing agent), then application of a U.S. Environmental Protection Agency (USEPA) chronic risk assessment model (e.g., PRG) is not appropriate or necessary.

C.2 BACKGROUND

For military sites that have restricted access, there exists the possibility that the site might be visited by unauthorized individuals (trespassers). In order to assess the potential health risks to such individuals, theoretical scenarios were developed based on approaches used in previous Department of Defense (DOD) risk assessments and on recommendations made by USEPA. Two trespasser scenarios are evaluated in this report; one considers adolescents (from age 7 up to and including 16; covering a 10-year exposure period) as the most likely trespassers (USEPA Region IV approach), and the second considers adult hunters or fishermen as being potential trespassers. In the latter case, the assumption is also made that the same individuals may be exposed as both adolescents (starting at age 7) and adults (starting at age 17 and continuing until age 30). Age 30 is selected as the endpoint because USEPA considers 30 years as a reasonable maximum residency period at any one location. Therefore, the total exposure duration for the adolescent/adult category is 23 years (i.e., starting at age 7 up to age 30).

C.3 METHOD

The general USEPA Region IX risk assessment methodology for deriving PRGs (see Sections 3.2.5 and 3.2.6) for industrial soil (USEPA, 1996b) and the USEPA Region III risk assessment methodology for deriving RBCs (see Sections 3.1.3 and 3.1.4) for industrial soil (USEPA, 1996a) will be used to calculate Health-Based Environmental Screening Levels for trespassers ($HBESL_{tres}$) for the chemical agents.

The Region IX method includes potential exposure by three routes: ingestion of soil, dermal contact, and inhalation of volatiles or particulates released from the soil. For noncancer endpoints, the algorithm for calculating a screening value for a trespasser is as follows:

$$HBESL_{tres} = \frac{THQ \times BW_t \times AT_n}{EF_t \times ED_t \times \left(\left(\frac{1}{RfD_o} \times \frac{IRS_t}{10^6\ mg/kg} \times FC \right) + \left(\frac{1}{RfD_o} \times \frac{SA_t \times AF \times ABS}{10^6\ mg/kg} \right) + \left(\frac{1}{RfD_i} \times \frac{IRA_t \times ET_t}{VF_s} \right) \right)} \quad \text{(C-1)}$$

where:

$HBESL_{tres}$	=	Health-based Environmental Screening Level for trespasser (mg chemical/kg soil)
THQ	=	Toxicity Hazard Quotient (=1)
BW_t	=	Body weight (kg)
AT_n	=	Averaging time, noncarcinogens (ED x 365 days/yr)
EF_t	=	Exposure frequency (days/yr)
ED_t	=	Exposure duration (yr)
RfD_o	=	Oral Reference Dose (mg chemical/kg body weight/day)
RfD_d	=	Dermal Reference Dose (mg/kg/day) **for Lewisite only** (see Section 9.2)
IRS_t	=	Soil ingestion rate (mg/day)
FI	=	Fraction ingested from contaminated source
SA_t	=	Skin surface area exposed (cm^2)
AF	=	Soil-to-skin adherence factor (mg/cm^2)
ABS	=	Skin absorption factor (%)
RfD_i	=	Inhalation Reference Dose (mg chemical/kg/day)
IRA_t	=	Inhalation rate (m^3/day)
ET_t	=	*Fraction of day spent at site*
VF_s	=	Chemical-specific volatilization factor for soil (m^3/kg)

According to USEPA guidelines, for contaminants having a Henry's Law Constant of less than 10^{-5} atm-m^3/mol, the Volatilization Constant in Equation C-1 is replaced with a default Particulate Emission Factor (PEF) of 1.32×10^9 m^3/kg (USEPA, 1996b). This applies to all the nerve agents. A PEF is also used for Lewisite because a chemical-specific Volatilization Factor (VF) cannot be calculated because a K_{ow} is not available. The inhalation of volatiles pathway was included for all the agents, even though the only agent of those evaluated in this report that may be expected to volatilize from subsurface soils is HD. Volatilization was considered to be a potentially important exposure pathway in the case of trespassers because of the possibility that the shortened exposure frequencies would allow for relatively high residual agent concentrations in soil.

For contaminants having a carcinogenic effect, the algorithm used to calculate a screening value for a trespasser is as follows:

$$HBESL_{tres} = \frac{THQ \times BW_t \times AT_c}{ED_t \times EF_t \times \left(\left(\frac{IRS_t \times CSF_o \times FC}{10^6\ mg/kg} \right) + \left(\frac{SA_t \times AF \times ABS \times CSF_o}{10^6\ mg/kg} \right) + \left(\frac{IRA_t \times ET_t \times CSF_i}{VF_s} \right) \right)} \quad \text{(C-2)}$$

where:

$HBESL_{tres}$	=	Health-Based Environmental Screening Level for trespasser (mg chemical/kg soil)
TR	=	Target cancer risk
BW_t	=	Body weight (kg)
AT_c	=	Averaging time for carcinogenic effects (70 yr)
ED_t	=	Exposure duration (yr)
EF_t	=	Exposure frequency (days/yr)
IRS_t	=	Soil ingestion (mg/day)
CSF_o	=	Oral slope factor [(mg/kg/day)$^{-1}$]
FI	=	Fraction ingested from contaminated source
SA_t	=	Skin surface area exposed (cm^2)
AF	=	Adherence factor (mg/cm^2)
ABS	=	Skin absorption factor (percent)
IRA_t	=	Inhalation rate (m^3/day)
ET_t	=	Fraction of day spent at site
CSF_i	=	Inhalation slope factor [(mg/kg/day)$^{-1}$]
VF_s	=	Volatilization factor fir soil, chemical-specific (m^3/kg)
PEF	=	Particulate emission factor for soil (1.32×10^9 m^3/kg)

Rationales for the exposure parameter values unique to the $HBESL_{tres}$ calculations are presented below. All the parameters used in Equations C-1 and C-2 are presented in Table C-1.

Dermal Reference Dose (RfDd). Derived for Lewisite using acute toxicity data (See Section 9.2).

Target cancer risk (TR). A discussion of the use of target cancer risk levels is given in Section 1.3.2 of this document. The target cancer risk level of 10^{-5} that is used for residential exposure scenarios is also considered appropriate for the trespasser scenarios.

Body weight (BW_t). USEPA Region IV considers the typical trespasser to be an adolescent 7-16 years old with a body weight of 45 kg (USEPA, 1995b). For the trespasser scenario for both adolescents and adults, an age span of 7-30 years and an average body weight of 60 kg is used in this report (estimated from age-specific body weight data provided in USEPA, 1989a).

Exposure Duration (ED_t). The only USEPA guidelines for selecting exposure duration values for trespassers is the default recommended by USEPA Region IV that the most likely adolescent trespassers would be 7-16 years old, resulting in a 10-year exposure duration. Other exposure durations may be more appropriate for specific sites. If a site includes habitat populated by game animals or includes lakes

or streams populated with fish, it may be attractive to hunters or fishermen. The possibility would then exist that the trespasser will be an adult and that the exposure duration will extend over a longer period of time, possibly as long as the individuals live in the area. Using the standard residential exposure duration of 30 years, an adolescent/adult trespasser exposure duration of 23 years is recommended (i.e., 10 years for adolescents age 7-16 and 13 years for adults age 17-30). The total 30-year period corresponds to the maximum reasonable residential duration from birth to age 30 at a single site.

Exposure Frequency (EF_t). USEPA Region IV notes that selection of trespasser exposure frequency should consider site-specific factors such as distance from the site to residences and the attractiveness of the site to the trespasser. For the purposes of this report, an exposure frequency of 12 days per year was chosen for the trespasser scenario. Other exposure frequencies may be more appropriate for specific sites, depending on climate, site accessibility, and the use of the site by hunters or fishermen.

Exposure Time (ET_t). There are no USEPA default values for the length of time that trespassers will remain at a given site. For the purposes of this report, an exposure time of 1 hour is used. Other exposure times may be more appropriate for specific sites.

Soil Ingestion rate (IRS_t). The standard default for daily soil ingestion by individuals older than 6 years is 100 mg/day, and this value is used here for soil ingestion by trespassers.

Fraction ingested from source (FI). This parameter reflects the percentage of daily ingested soil that contains the chemical agent of concern. Since the IRS_t reflects the daily rate of soil ingestion, it includes ingestion of soils and dusts from sources outside of the restricted area. It is assumed here that 50% of the daily ingested soil will come from the site.

Skin surface area exposed (SA_t). For the adolescent trespasser scenario used in this report, an exposed skin surface area of 4300 cm^2, the median value between children and adults, is used. For the adolescent/adult trespasser, an exposed skin surface area of 5000 cm^2, the median value between adolescents and adults, is used.

Table C-1. Values used for calculating trespasser HBESLs

Parameter	Value	Source	Comment/Reference
THQ	1	USEPA	Standard USEPA value (RAGs Part A, 1989; Part B, 1991a)
RfD_o	Chemical-specific	Army	Interim standard (Army Office of the Surgeon General, August 1, 1996; see Table 1-2).
RfD_i	Chemical-specific	Army	Derived from Air Exposure Limits (see Table 1-2) adopted by DHHS (1988) and by the Army (DA, 1990; 1991) using an inhalation rate of 20 m^3/day and a body weight of 70 kg.
RfD_d	Chemical-specific	Army	Used for Lewisite only. Derived from acute toxicity data (see Sections 1.2 and 9.2).
CSF_o	Chemical-specific	Army	See Table 1-2.
CSF_i	Chemical-specific	Army	See Table 1-2.
TR	10^{-5}	Army	The recommended range of values is 10^{-4} to 10^{-6} (RAGs part A). A TR of 10^{-5} is used in this report for residential exposures (see Section 1.3.2)
BW	45 kg 60 kg	Army	Adolescents (see text) Adolescents/adults (see text)
AT_c	25,550 days	USEPA	The AT for carcinogenic risks is assumed to be over a lifetime (70 yr) because it is the additional risk averaged over the lifetime of the individual(s) exposed (RAGs, Part A).
AT_n	ED	USEPA	For noncarcinogenic risks the AT equals the duration of exposure (ED) (RAGs Part A and Part B)
EF_t	12 days/yr	Army	See text
ED_t	10 yr 23 yr	Army	Adolescents (see text) Adolescents/adults (see text)
ET_t	1 hr	Army	See text
IRS_t	100 mg/day	Army	Standard USEPA default for soil ingestion by adults
FI	0.5	USEPA	Fraction of daily soil ingested from site
SA_t	4300 cm^2 5000 cm^2	Army	Adolescents (see text) Adolescents/adults (see text)
ABS	Chemical-specific	Army	For 12-hour period (see Table 2-4)
AF	0.08 mg/cm^2	USEPA	This value is used for adults by USEPA Region IX
IRA_t	20 m^3/day	Army	Standard USEPA default for adults
VF	Chemical-specific	Army	Calculated using USEPA recommended methods (see Table 2-3)
PEF	1.32×10^9 m^3/kg	USEPA	Standard USEPA default (USEPA, 1996c)

C.4 RESULTS

The trespasser HBESL values calculated with Equations C-1 and C-2, using the toxicity values listed in Table 1-2 and the exposure parameters listed in Table C-1, are summarized in Table C-2. To use these values as an action/no action tool, the application criteria bulleted below must be met. In addition, the user should be familiar with the key uncertainties (identified in Table C-3) in the assessment model and type of effect. In this type of scenario, types of 'action' that may be determined to be necessary include additional management/engineering controls, treatment to further minimize potential for repeated/long-term exposure, or site-specific risk assessment to ascertain specific exposure conditions.

Target risk levels are acceptable

This can only be assessed through negotiation with applicable regulators and other stakeholders (see Section 1.3.2).

Assumptions made in these scenarios are at least equally conservative if not more conservative than site-specific assumptions.

For example, if a site-specific scenario includes an exposure frequency of more than 12 days/yr, then the HBESL assumption may be considered under-conservative.

Exposure frequency and duration represent a chronic exposure.

Since exposure durations and frequencies cited in the example may not be realistically considered a significant chronic or even subchronic exposure, the application of a chronic risk model may be inappropriate. In such cases acute toxicity should be evaluated separately (see Section C.5).

A single chemical agent is of concern.

Table C-2. Calculated $HBESL_{tres}$ values for chemical warfare agents

Agent (mg/kg soil)	Scenario	PRG (noncancer)	PRG[a] (cancer)	RBC (noncancer)	RBC[a] (cancer)
HD	adolescent	119[b]	19[b]	192	249
	adolesc./adult	150[b]	11[b]	256	144
Lewisite	adolescent	66	-	27*	-
	adolesc./adult	76	-	36*	-
GA	adolescent	451[b]	-	1095	-
	adolesc./adult	583[b]	-	1460	-
GB	adolescent	225[b]	-	548	-
	adolesc./adult	294[b]	-	730	-
GD	adolescent	42[b]	-	110	-
	adolesc./adult	54[b]	-	146	-
VX	adolescent	13[b]	-	16.4	-
	adolesc./adult	17[b]	-	21.9	-

[a] Target cancer risk level of 10^{-5}

[b] Inhalation of vapors included in calculation

* Calculated values decreased by a factor of 100 to compensate for possibility of acute toxicity (see text)

Table C-3. Uncertainty Summary - Key Areas of Uncertainty and Type of Effect* on "Conservatism" of $HBESL_{tres}$	
Type of Uncertainty	**Type of effect**
Inhalation slope factor (CSF_i)	Possible over conservatism because of route-to-route extrapolation
Multiple exposure pathways (PRG)	Possible over conservatism, especially for vesicants HD and Lewisite
Exposure duration (ED_t)	Unknown - possible over/under conservatism
Exposure frequency (EF_t)	Unknown - possible over/under conservatism
Exposure time (ET_t)	Unknown - possible under conservatism
Skin surface area exposed (SA)	Unknown - depends on climate and season of the year
Fraction ingested from contaminated source (FI)	Unknown - possible over/under conservatism
Acute toxicity	Possible under conservatism, but compensated for by using an adjustment factor of 10

* *Type of effect has been determined by professional judgement*

C.5 $HBESL_{tres}$ COMPARISONS WITH ACUTE TOXICITY DATA

Because the calculated $HBESL_{tres}$s are extrapolations from chronic toxicity values to relatively short-term exposures, care must be used to ensure that the resulting criteria are not set at levels at which acute toxic effects might occur. The chronic risk assessment model may fail to accommodate the 'acute' risk from a single 'hotspot' of concentrated chemical agent. In situations where the calculated HBESL is at levels which approach potential acute toxicity concerns, it may be more prudent to consider the assessment of individual hotspots to ensure that the potential of acute risk is mitigated at these higher concentration levels. *Only in situations where the agent is reasonably assumed to be homogeneously* adsorbed or otherwise mixed in with the matrix (e.g. possibly waste soil or even more homogenous as in liquid matrices) is the use of the risk assessment model appropriate.

In this section the potential exposures at the trespasser HBESLs are compared to experimental human and animal data identifying no-effect and minimum effect levels (MELs) for acute exposures. The acute toxicity data are summarized in more detail in Section 1.3.8. It should be noted that the potential for acute toxicity is dependent on the values used for the exposure parameters.

Agent HD. The maximum $HBESL_{tres}$ is 256 mg HD/kg soil for adolescents/adults. At this HBESL, the dose resulting from the incidental ingestion of 50 mg of soil is approximately 0.0013 mg HD (0.0002 mg/kg body weight). In studies conducted on rats, a dose of 0.03 mg/kg/day (about 0.01 mg/animal) caused no toxic effects or produced only mild signs of toxicity after repeated exposures for 13 weeks (see Section 1.3.8).

Assuming an exposed skin area of 5000 cm^2 for adolescent/adult trespassers, and a soil-to-skin adherence of 0.08 mg per cm^2 of skin, the amount of soil that may be in contact with the skin is 400 mg and, at the maximum $HBESL_{tres}$ of 256 mg/kg, this quantity of soil would contain about 0.1 mg of HD (256 mg/kg x 1 kg/1,000,000 mg x 400 mg). The average amount of HD per square centimeter of

exposed skin would be 0.02 µg (0.01 mg/5000 cm^2). In human experimental studies application of 2.5 µg of HD to the skin resulted in erythema, in 87 of 209 individuals and blistering in 5 of 209 (see Section 1.3.8). These data indicate that the minimum effect level may be less than 1 µg; in comparison, at the HBESL, the estimated average exposure is 0.02 µg/cm^2 (and it would be about one-tenth of this value for the cancer-based $HBESL_{tres}$ values). These HBESLs would be marginally protective of acute percutaneous exposures, but only if the agent is uniformly dispersed in the soil. The $HBESL_{tres}$ values should not be applied to situations where the HD is concentrated in "hotspots" or where globules of agent are encapsulated in a polymeric coating formed by the HD hydrolysis products (see Section 1.2.3).

The HBESL (256 mg/kg) could theoretically result in an HD air concentration of 0.005 mg/m^3, assuming that the air concentration is a function of the soil concentration (256 mg/kg) divided by the VF (5.62 x 10^4 m^3/kg). A CT of 12 mg-min/m^3 (0.2 mg/m^3 for 60 min) has been reported to be a no-effect level for eye irritation (see Section 1.3.8). The maximum allowable CT for skin effects is 5 mg-min/m^3 and that for eye effects is 2 mg-min/m^3 (DA, 1974); these values equate to 0.08 and 0.03 mg/m^3, respectively, for 60-min exposures. Therefore, for the presumed conditions of exposure for the trespasser scenario (i.e., 1-hr exposure time), if the resulting air concentration is no greater than 0.0005 mg/m^3, then the HBESLs appear to be sufficiently protective against the possibility of vapor effects to the skin or eyes.

Agent VX. The maximum $HBESL_{tres}$ is 22 mg VX/kg soil for adolescent/adults, and the dose resulting from the incidental ingestion of 50 mg of soil would be approximately 0.0001 mg VX. In tests on humans, an oral dose of about 0.1 mg (calculated from a reported dose of 0.0014 mg/kg/day and a default body weight of 70 kg) caused no signs of toxicity even after 7 days of exposure (see Section 1.3.8). This dose is about 100 times greater than that estimated from the maximum soil $HBESL_{tres}$, under the assumed conditions of exposure.

VX is not very volatile; therefore, the percutaneous and oral exposures are expected to be much more significant than the inhalation exposure. Assuming an exposed skin area of 5000 cm^2 for adolescent/adult trespassers, and a soil-to-skin adherence of 0.08 mg per cm^2 of skin, the amount of soil that may be in contact with the skin is 400 mg and, at the $HBESL_{tres}$ of 22 mg/kg, this quantity of soil would contain about 0.009 mg of VX [22 mg/kg x (1 kg/1,000,000 mg) x 400 mg = 0.009 mg VX]. In comparison, DA (1974) reported that 0.32 mg of liquid VX applied to the forearm resulted in mild signs of toxicity in 1% of the tested individuals. Therefore, acutely toxic effects are not likely at the HBESL, under the stated conditions of exposure.

Agent GB. The maximum $HBESL_{tres}$ is 730 mg GB/kg soil for adolescent/adults, and the dose resulting from the incidental ingestion of 50 mg of soil would be approximately 0.037 mg GB. In tests on humans, an oral dose of about 1.54 mg (based on a reported dose of 0.022 mg/kg/day and a default body weight of 70 kg) caused mild signs of toxicity (see Section 1.3.8). A dose of 0.15 (based on a reported dose of 0.002 mg/kg/day and a default body weight of 70 kg) caused only excessive dreaming and talking in sleep (see Section 1.3.8). Therefore, the $HBESL_{tres}$ would appear to be protective for acute oral toxicity under the stated conditions of exposure.

Assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5000 cm^2, the total amount of soil on the skin would amount to 400 mg. At the maximum $HBESL_{tres}$ of 730 mg

GB/kg soil for adolescent/adults, 0.3 mg of GB would be in contact with the skin [730 mg/kg x (1 kg/1,000,000 mg) x 400 mg = 0.3 mg GB]. In comparison, it has been reported that 20-50 mg of GB applied to the skin will not result in signs of toxicity (see Section 1.3.8); therefore, the soil $HBESL_{tres}$ levels should be protective of acute dermal exposures for the stated conditions of exposure.

A soil HBESL of 730 mg/kg soil could theoretically result in a GB air concentration of 0.004 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (730 mg/kg) divided by the VF (1.7×10^5 m^3/kg). The estimated no-effect concentration for a 60-min exposure to GB is 0.02 mg/m^3 (see Section 1.3.8), therefore, it is unlikely that the soil trespasser HBESLs would result in an acutely toxic vapor concentrations, for the assumed conditions of exposure.

Agent GA. The maximum $HBESL_{tres}$ is 1460 mg/kg for adolescents/adults. At this HBESL, the dose resulting from ingestion of 50 mg of soil is about 0.07 mg GA. A minimum effect level in humans is estimated to be 0.37 mg (see Section 1.3.8); therefore, the soil $HBESL_{tres}$ levels are expected to be marginally protective for acute toxicity resulting from incidental ingestion of soil, for the stated conditions of exposure.

At the maximum $HBESL_{tres}$ of 1460 mg/kg soil for adolescent/adults, and assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5000 cm^2, the total amount of soil on the skin would amount to 400 mg and would contain 0.6 mg of GA [1460 mg/kg x (1 kg/1,000,000 mg) x 400 mg = 0.6 mg GA]. In comparison, it was estimated that the minimum effect level for dermal exposures is 32-48 mg, and experimental data suggest that it may be as high as 300 mg (see Section 1.3.8). This is substantially greater than the maximum dermal dose for trespassers; therefore, the soil $HBESL_{tres}$ levels would appear to be protective of acute dermal exposures for the stated conditions of exposure.

A soil HBESL of 1460 mg/kg soil could theoretically result in a GA air concentration of about 0.006 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (1460 mg/kg) divided by the VF (3.8×10^5 m^3/kg). In comparison, a no-effect level of 0.05 mg/m^3 has been estimated by extrapolation from toxicity data for GB (see Section 1.3.8). The soil trespasser PRGs for GA would therefore not be expected to result in an acutely toxic vapor concentration.

Agent GD. The maximum $HBESL_{tres}$ is 146 mg/kg for adolescent/adults. At this HBESL, the dose resulting from ingestion of 50 mg of soil is about 0.007 mg GD. A minimum effect level in humans is estimated to be 0.09 mg for oral exposures (see Section 1.3.8); therefore, the trespasser HBESL is expected to be marginally protective for acute toxicity resulting from ingestion of soil, for the stated conditions of exposure.

At the maximum $HBESL_{tres}$ of 146 mg GD/kg soil for adolescents/adults, and assuming a soil adherence of 0.08 mg per cm^2 of skin and a total exposed skin area of 5000 cm^2, the total amount of soil on the skin would be 400 mg and would contain 0.05 mg of GD [146 mg/kg x (1 kg/1,000,000 mg) x 400 mg = 0.05 mg GD] . In comparison, it has been estimated that the minimum effect level for dermal exposures is 11 mg (see Section 1.3.8). Therefore, the trespasser HBESLs for GD are expected to be protective for acute dermal exposures for the stated conditions of exposure.

A soil HBESL of 146 mg/kg soil could theoretically result in a GD air concentration of 0.0009 mg/m^3, assuming that the air concentration can be estimated from the soil concentration (146 mg/kg) divided by the VF (1.7×10^5 m^3/kg). In comparison, a 1-hour no-effect level of 0.013 mg/m^3 has been estimated by extrapolation from toxicity data for GB (see Section 1.3.8); therefore, the soil $HBESL_{tres}$ would not be expected to result in acutely toxic vapor concentrations for the stated conditions of exposure.

Lewisite. The maximum calculated $HBESL_{tres}$ for Lewisite is 3650 mg/kg for adolescent/adults. At a soil HBESL of 3650 mg/kg, the dose resulting from ingestion of 50 mg of soil is 0.2 mg (0.003 mg/kg body weight). Estimates of MELs for orally administered Lewisite in laboratory animals range from 0.07 to 2 mg/kg (see Section 1.3.8). This is equivalent to dose range of 0.02 to 0.6 mg per animal. The $HBESL_{tres}$ calculated using the RBC methodology may therefore not be protective for the stated conditions of exposure. To accommodate for potential acute effects the RBC_{tres} values were adjusted by a factor of 100 (see Table C-2). The resulting HBESLs of 27 and 36 mg/kg would correspond to an ingested dose of about 0.001 and 0.002 mg and would be expected to be marginally protective of acute oral toxicity.

In calculating the Lewisite PRGs for trespassers, a dermal RfD of 0.0000017 mg/kg was used (see Section 9.2 for derivation). The resulting $HBESL_{tres}$ values are 66 mg/kg soil for adolescents and 76 mg/kg for adolescent/adults. At the HBESL of 76 mg/kg, and assuming a soil adherence of 0.08 mg per cm^2 and a total exposed skin area of 5000 cm^2, the total amount of soil on the skin would be 400 mg and would contain about 0.03 mg of Lewisite. The average concentration of Lewisite on the skin would be 0.000006 mg/cm^2 (0.03 mg/5000 cm^2 = 0.000006 mg/cm^2). Minimum effect levels (MELs) for percutaneous exposures to Lewisite were not found in the available literature. The median threshold dose for blistering was reported to be about 14 μg, and a dose of 3.5 μg resulted in erythema in 29 of 93 individuals and blistering in 8 of 93 (see Section 1.3.8). The MEL and no-effect level are likely to be below 1 μg. The estimated percutaneous exposure at the HBESL of 76 mg/kg is 0.006 $\mu g/cm^2$, therefore, the HBESLs are expected to be protective under the stated conditions of exposure.

A soil VF cannot be calculated for Lewisite because of its instability. Therefore, in the HBESL equation, the VF is replaced with the particulate emission factor (PEF = 1.32×10^9 m^3/kg) to account for exposures through fugitive dust emissions. These HBESLs would also be appropriate for soil containing the nonvolatile breakdown products of Lewisite. A VF is available for one of the breakdown products, 2-chlorovinylarsonous acid (see Appendix I).

C.6 CONCLUSIONS

As originally stated, though access to military installations is restricted, some instances of exposure of trespassers to residual chemical agent may occasionally occur. In most cases, these infrequent occurrences are not sufficient to warrant concern regarding a potential chronic risk. However, in those situations where there is a potential concern for repeated exposures to agent residues, the chronic exposures risk model and $HBESLs_{tres}$ described above may be a useful mechanism to determine if additional management/ engineering controls, treatment, or a more site-specific risk assessment are warranted.

This scenario demonstrates that the chronic risk assessment model may fail to accommodate the 'acute' risk from a single 'hotspot' of concentrated chemical agent. In situations where the calculated HBESL is at levels which approach potential acute toxicity concerns, it may be more prudent to consider the assessment of individual hotspots to ensure that the potential of acute risk is mitigated at these higher concentration levels. Only in situations where the agent is reasonably assumed to be homogeneously adsorbed or otherwise mixed in with the matrix (e.g., possibly waste soil or even more homogenous as in liquid matrices) is the use of the risk assessment model appropriate.

APPENDIX D

AGRICULTURAL/GRAZING SCENARIOS

The possibility exists that lands currently under the control of the Army will be leased for agricultural or grazing purposes. If chemical agent materials had at some time been disposed of on such lands, it would be necessary to certify that any residual amounts of material in the soil would be safe to the individuals involved in the above mentioned activities. The screening levels that would be appropriate for such uses would be dependent on several factors, the major one being whether any civilian populations actually resided on the land. In such cases residential Health-Based Environmental Screening Levels (HBESLs) could be used for such sites if appropriately modified to account for any unusual exposure routes or enhanced exposure through those exposure routes already addressed in the residential HBESLs.

Ingestion of fruits and vegetables. For example, one unique exposure route might be the ingestion of contaminated fruits or vegetables grown on the site. With the exception of sulfur mustard (HD), most of the chemical agents considered in this document have soil half-lives that are very short (see Table 2-3). Furthermore, the log K_{ow} values for the agents are relatively small (see Table 2-3) indicating a very low potential for bioaccumulation. Therefore, uptake of these agents into fruit or vegetables and/or the bioaccumulation through the food chain into farm animals is highly unlikely.

Although the potential for bioaccumulation of HD is low, bulk amounts of this agent can have a relatively long soil half-life when individual globules become encased by a oligomeric coating (formed with the hydrolysis products of HD) which prevents further dissolution and degradation. In this state encapsulated HD can remain in soil for many years, and the possibility exists that the agent may be released during farming operations. Under such circumstances, HD may be transferred into the air as vapors, or in windblown dust. Deposition on food crops is a theoretical, although very remote, possibility.

Inhalation and dermal exposure. As noted above, encapsulated HD can be sequestered in soil for many years. If the HD capsules are broken open, farm workers could be exposed through dermal contact, inadvertent soil ingestion, and inhalation of vapors or dust particulates. In such cases, the potential for acute exposures is much higher than in the scenarios used to establish the standard HBESL values. HBESLs cannot be established for such situations, and the necessary steps must be taken to ensure that HD is not present in encapsulated form.

Ground water. Because farm families may utilize well water as a source of drinking water, and because such water may not undergo standard water treatment procedures, ingestion of tapwater may be a very important exposure pathway for some types of contaminants. However, as discussed in Section 1.3.3 and Appendices E and H, the migration of chemical warfare agents through the soil to the underlining aquifer is considered to be highly unlikely. This is due primarily to the relatively rapid rates of degradation and/or to the immobility of the agent (as in the case of encapsulated HD). Because of their longer soil persistence times, and because they are generally more mobile in soils, the breakdown products of the chemical warfare agents are likely to have a greater potential for ground-water contamination than the agents themselves.

Grazing. The potential for long-term exposure to chemical agents on lands used for grazing is probably very low. As mentioned above, there is no evidence that any of the agents will bioaccumulate through the food chain. Furthermore the frequency, duration, and magnitude of exposure through dermal contact, inadvertent soil ingestion, and inhalation of vapors or particulates, is likely to be considerably less for ranchers than for farmers. The derivation of HBESLs for ranchers would be dependent on the selection of realistic values for the appropriate exposure parameters. It seems logical, however, that the HBESLs for ranchers would fall somewhere above those for trespassers and below those for industrial workers, and the use of the latter values would be a conservative approach.

APPENDIX E

MODELING POTENTIAL CHEMICAL AGENT CONTAMINATION OF GROUND WATER

E.1. OBJECTIVE

The general Army opinion is that chemical agents, because of their instability and volatility, will not remain in the environment long enough to contaminate ground water. The soundness of this opinion, however, has not until now been tested through the application of computer modeling to data.

The objective of this appendix is to model the potential for chemical agents to contaminate ground water in two generic climatic/geologic/contamination scenarios. The results will be in the form of horizontal distances from a site, beyond which any agents in ground water would be at or below predetermined evaluation endpoint concentrations (see Section E.4) .

E.2 CONCEPTUAL MODEL AND SOFTWARE USED

Chemical agent in soil will either volatilize into the air, adsorb onto organic soil constituents or dissolve into soil water. Infiltrating water passes by the agent, which dissolves (according to chemical-specific solubility factors) into liquid phase and travels vertically through the vadose (unsaturated) zone if field capacity is exceeded, until it reaches the water table (saturated zone). While traveling vertically, a portion of dissolved agent will continue to adsorb onto available organic material and volatilize into pore-air. This state of dynamic equilibrium is defined according to aspects of the infiltrating water, as well as chemical- and soil-specific characteristics. Upon reaching the water table, infiltrating water (or recharge) begins flowing generally horizontally along aquifer flow lines, transporting the remaining agent with it. While in liquid phase (i.e. while traveling vertically or horizontally), agent degrades through hydrolysis.

The software applied in this appendix includes a combination of VLEACH to model leaching from the vadose zone to ground water and a model developed by the U.S. Army Center For Health Promotion and Preventive Medicine (USACHPPM) for movement of the compounds after they enter the aquifer. VLEACH (Version 2.2a) is a one-dimensional finite difference vadose zone leaching model developed for the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency (USEPA) (Ravi and Johnson, 1996). It is based on the original VLEACH (version 1.0) developed for USEPA Region IX in 1990. The model estimates the impact on underlying ground water of the mobilization and migration of sorbed organic pollutants located in the vadose zone. VLEACH has been used to evaluate impacts of volatile organic contaminants at the Phoenix-Goodyear

Airport Superfund site (Rosenbloom et al, 1993). Subsequently it has been used at numerous other sites. VLEACH and its documentation were obtained from the website of the USEPA's Center for Subsurface Modeling Support (http://earth1.epa.gov/ada/models.html).

The second model, covering flow in the aquifer (i.e., horizontal flow), computes the amount of time required for a given concentration of chemical agent that reaches the vadose zone to hydrolyze to a specified concentration, in this instance the evaluation endpoint concentration for that agent (see Section E.4). This time is then multiplied by ground-water flow rate to calculate a horizontal distance from the source. Figure E-1 presents the equations used.

Figure E-1: Equations to compute time needed for compound to hydrolyze to evaluation endpoint concentration

If A(t) = amount of compound remaining at any time, then $dA/dt = kA$,

where:

$k = \frac{-\ln 2}{t_{1/2}}$

k = constant of proportionality

t = time

$t_{1/2}$ = half-life

FR = starting concentration/ endpoint concentration

$t = \frac{-\ln FR}{k}$

SOURCE: Zill, D.G., A First Course in Differential Equations, PWS-Kent Publishing, Boston, 1993

The chemical-specific parameters that were applied for the different chemicals in the VLEACH simulations are shown in Table E-1. Except for sulfur mustard (HD) and Lewisite, the hydrolysis half lives were taken from Table 1-1. The average hydrolysis rate is the geometric mean of all half-life values listed for each chemical. Table 1-1 listed a range for the hydrolysis half life of HD. The mean for HD, therefore is the arithmetic mean of the high and low values of the range presented, instead of the geometric mean of the three data points that were known. The fastest and slowest hydrolysis half-lives for HD are the lower and upper bounds of the listed range. Table 1-1 lists no estimate of the hydrolysis half-life for Lewisite. It states that the "solubility data are meaningless [for Lewisite] because of very rapid hydrolysis which is limited by rate of dissolution (Rosenblatt et al., 1975)." The average of 0.005 day assumed for Lewisite is thus highly conservative; the average rate, for example, is still larger than the fastest rate for HD, which, though fast, was slow enough to be measurable. The fastest and slowest hydrolysis rates for Lewisite are arbitrarily considered to be one order of magnitude higher and lower, respectively, than the average.

Table E-1. Chemical-specific parameters

Agent	Organic carbon distribution coefficient (mL/g)	Henry's constant (dimensionless)	Water solubility (mg/L)	Free air diffusion coefficient (m^2/day)	Hydrolysis rates (half-lives in days) Slowest	Average	Fastest
HD	133.0	0.00098	920	0.8554	0.0108	0.0067	0.0027
VX	327.0	0.00000033	30000	0.536	83.333	8.945	2.083
GB	34.6	0.000022	1090000	0.864	10.417	0.4186	0.02083
GA	38.5	0.00000623	98000	0.79488	0.3542	0.1563	0.0833
GD	234.0	0.000187	21000	0.70848	2.5	0.8664	0.0375
Lewisite	2.88	0.013	500	0.85536	0.05	0.005	0.0005

Because of its rapid hydrolysis, no estimate of the organic carbon distribution coefficient (K_{oc}) could be calculated for Lewisite. Since several essential parameters are not available to derive K_{oc} for Lewisite, the only approach that seemed possible was to make a worst-case estimate. Accordingly, the K_{oc} was assumed to be one order of magnitude lower than the smallest K_{oc} of the other five chemicals. Because GB is miscible, the solubility was arbitrarily assumed to be 1.09 x 10^6 mg/L, which is the same as its liquid density. Assuming a solubility of 1.00 x 10^6 mg/L (as considered in another approach[1]) would yield only a slightly smaller estimate of GB's solubility in water. The choice was made to use the more conservative number.

E.3 SCENARIO CHARACTERIZATIONS

Data from lithologic and hydrologic studies of the Edgewood Area of Aberdeen Proving Ground (USGS 1996) and the Tooele Army Depot (State of Utah, 1981; James M. Montgomery, 1987) were used to generate two generic landscape/climate scenarios. These were called the humid climate and arid climate scenarios, respectively. In addition to the landscape and rainfall parameters listed in Table E-2, the humid climate is defined as having a water table 3.7 meters (12 feet, per USGS 1996) below the ground surface, and the arid climate is defined as having a water table 59 meters (194 feet, per State of Utah 1981) below ground surface. Parameter values were chosen to correspond with a vadose zone comprised entirely of sand. This would tend to maximize agent transport and thereby produce a conservative estimate of ground-water contamination (for the purposes of risk assessment). The rates of flow (approximately horizontal) of ground water in the humid climate and arid climate scenarios were assumed to be 0.13 meter/day (per USGS 1996) and 1.22 meters/day (per James M. Montgomery, 1987), respectively.

[1] Small (1984) recommends solubility = 1 x 10^6 mg/L if known to be infinitely soluble in water.

Hydrogeologic parameters such as depth to water table and ground-water flow rate can vary widely. Because of this, and to investigate the potential effects of individual parameters, the arid climate was also modeled with a water table depth of 3.7 meters (to demonstrate the effects of water table depth on an otherwise identical scenario), and again with the 3.7-meter depth and a ground-water flow rate of 0.13 meters/day. Both parameter values were taken from the humid climate. To further investigate the sensitivity of the agent VX in the arid scenario to soil organic carbon content and depth to water table, additional runs of the models were performed with varying levels of soil carbon and water table depth.

Table E-2. Landscape parameters used in VLEACH modeling

Parameter	Values used in humid scenario	Values used in arid scenario
recharge rate	0.46 meters/year	0.09 meters/year
dry bulk density	1.65 g/cm^2	1.65 g/cm^2
effective porosity	0.354	0.354
volumetric water content	0.177	0.09
saturation of soil	50%	25.4%
soil organic carbon content	0.0071	0.001
annual rainfall (used as one of several factors to estimate the recharge rate).	1.07 meters/year	0.55 meters/year

Documentation for VLEACH indicates that the fraction of organic matter in sand is 0.0071, which is used for the value in the humid climate. The organic content of the soil was assumed to be 0.001 for the arid climate to account for both a lower biologic activity (and therefore lower organic input to soil) and extreme depth to the water table (there generally being less organic matter at deeper depths) in arid regions.

In addition to the two landscapes modeled, the following two contamination scenarios were modeled; the "remediated" scenario and the "leak" scenario. In both cases, the top 1.22 meters (4 feet) of soil are uncontaminated, the next 0.61 meters (2 feet) of soil are contaminated, and the remainder of soil above the water table (57.3 meters or 1.83 meters for the arid climate, 1.83 meters for the humid climate) is uncontaminated at the start of the run of the model (i.e., at t_0).

The remediated scenario is a hypothetical site of a past remediation project where any agents found will be at concentrations no higher than the HBESL for industrial sites, as listed in Table 11-2. The contaminated zone has an area of 92.9 square meters (1,000 square feet), and at t_0 it is uniformly contaminated at the concentration listed as the industrial soil HBESL for each chemical (e.g., .85 mg VX/kg soil). There are, therefore, 56.7 m^3 of soil that are uniformly contaminated. It is assumed that the

entire quantity of agent seeping into the ground water on a given day dissolves into 1000 L of water at the exact starting point for application of the horizontal flow model. Because hydrolysis is occurring as ground water moves across the water table directly beneath the contaminated zone of 1000 ft^2, this method should greatly overestimate the true concentration at the starting point for the horizontal-flow model.

In the simulated leak, the contaminated zone has an area of 0.09 square meters (1 square foot), and at t_0 it is uniformly contaminated with 500,000 mg of chemical per kg of dry soil. There are, therefore, 0.06 m^3 (2 ft^3) of soil uniformly contaminated. It is assumed that the entire quantity of agent seeping into the ground water on a given day dissolves into 1 L of water. If a buried chemical munition would suddenly start to leak, it would likely take many days for equilibrium to be reached at 500,000 mg/kg. Simultaneous hydrolytic degradation would further slow, and possibly deny, attainment of equilibrium. Thus, the described situation will likely considerably overestimate the possible agent source.

E.4 DERIVING AN EVALUATION ENDPOINT

It is necessary to define for the modeling a non-zero, positive concentration value that describes a 'no-risk' level of agent. For those situations where an open drinking water source is initially contaminated (either through accidental or intentional release), initial evaluation of the associated risks may involve comparison with the Army's Field Drinking Water Standards (FDWS) (DA 1996b). These values were derived to ensure adequate protection of a healthy male military population consuming 5-15 L of water per day for up to 7 days. While the soldier consumption rate is significantly larger than the USEPA assumption of 2 L/day for the general civilian population, individuals within the civilian population (such as elderly and children) may be somewhat more susceptible to agent toxicity than the military population, and the USEPA default assumption for exposure duration is much longer (30 years). Therefore, to ensure an extremely conservative evaluation, the worst case assumption of potential long-term contamination of a general population water supply was used in determining agent concentration endpoints for the model.

E.4.1 Method of Derivation

The EPA Region IX PRG risk assessment methodology for tapwater (USEPA, 1996b) can be used to calculate evaluation endpoint concentrations for the chemical agents. These extremely conservative values can then be used to simulate an extreme worst case agent migration scenario. The Region IX method includes potential exposure by two pathways: ingestion of drinking water and inhalation of volatiles that might be released from tapwater during routine household activities.

For noncarcinogenic endpoints, the algorithm used for calculating an evaluation endpoint for ground-water modeling is as follows:

$$PRG_{dw} = \frac{THQ \times BW \times AT_n \times 1000\ ug/mg}{EF \times ED \times \left(\frac{IRW}{RfD_o} + \frac{VF_w \times IRA}{RfD_i}\right)}$$

For contaminants having a carcinogenic effect, the algorithm used for calculating an evaluation endpoint for ground-water modeling is as follows:

$$PRG_{dw} = \frac{TR \times AT_c \times 1000\ ug/mg}{EF\ [\ (VF_w \times InhF_{adj} \times CSF_i) + (IFW_{adj} \times CSF_o)\ ]}$$

The values of several of the listed parameters, including the toxicity values (reference doses (RfDs) and cancer slope factors (CSFs)), averaging times for carcinogenic and noncarcinogenic effects (AT_c and AT_n), body weight (BW), exposure duration (ED), and inhalation rate (IRA), are the same as those used in the HBESL calculations for residential scenarios presented elsewhere in this document. Other exposure parameters are more specific to the tapwater scenario as described by EPA Region IX guidance. The unique additional exposure assumptions used to calculate values for the agents are presented below.

Volatilization Factor (VF). Health risks associated with inhalation of chemicals indoors are relevant only for chemicals that easily volatilize from water during household activities such as showering, laundering, and dish washing. The PRG screening levels for tapwater incorporate a volatilization factor (VF_w) that is applicable only to volatile chemicals. According to EPA criteria, only sulfur mustard is considered volatile (please see Sec. 1.3.6 for a more detailed discussion of EPA criteria for defining volatility). It should be noted, however, that hydrolysis of HD is very rapid (half-life 0.08 hr), and trace amounts of HD would not be stable in water. Therefore, volatilization from water (and therefore the inhalation pathway) is not likely to be significant.

The USEPA criterion for volatility is used only to identify those chemicals for which the inhalation pathway should be considered when deriving PRGs (USEPA, 1991a). USEPA (1991a) reported that the experimental data of Andelman (1990), which defined the relationship between the concentration of a chemical in tapwater and its concentration in indoor air (based on data for radon), included a default volatilization constant of 0.5 L/m³. This is the volatilization factor that is used to derive PRGs for tapwater.

Inhalation rate and age-adjusted inhalation factor (IRA, $InhF_{adj}$). As noted above, the inhalation pathway is not expected to be a significant source of exposure for any of the agents based on their Henry's Law Constants or rapid rate of very rapid hydrolysis (agent HD). Therefore, the inhalation pathway is not included in the calculations for evaluation endpoints.

Ingestion of tapwater and tapwater-based drinks (IRW). For the tapwater exposure pathway, the standard USEPA default for drinking water consumption is 2 L/day for adults. An intake rate of 2 L/day

is considered a maximum value (approximately the 90th percentile), and 1.4 L/day is considered a reasonable estimate of the average daily intake (USEPA, 1989a). USEPA currently uses 1 L/day as the default value for children. For ingestion of tapwater and water-based drinks, USEPA estimated that 75 to 100% of such intake would occur at the place of residence (USEPA, 1989a). For calculating screening levels, the conservative assumption is made that consumption of tapwater and water-based drinks occurs entirely at the place of residence.

E.4.2 Derivation Results

The calculated evaluation endpoint values to be used in modeling in this appendix include: 0.087 μg/L for HD (based on cancer risk level of 10^{-5}); 0.022 for μg/L GA; 0.73 for μg/L GB; 1.5 μg/L for GD; and 0.15 μg/L for VX; and 3.7 μg/L for Lewisite.

E.5 RUNNING THE MODELS

Model runs were performed on each agent individually, in all climate/scenario combinations (arid remediated, arid leak, humid remediated, humid leak) at each rate of hydrolysis (fastest, average, and slowest), for a total of 12 runs per agent. Additional runs were performed with an altered arid climate, for all scenarios and hydrolysis rates, totaling an additional 12 runs per agent. Also, as mentioned earlier, 5 additional runs were performed on an altered arid climate "leak" scenario for agent VX, varying soil carbon and depth to ground water.

VLEACH modeled the movement of contamination (incorporating adsorption but not considering hydrolysis) and estimated the number of grams of chemical reaching the water table on each ensuing day. This concentration was then put through independent calculations of exponential decay to determine how much agent, minus the portion hydrolyzed during vertical flow, actually enters ground water. The output from a complete run of VLEACH is too large to include in this appendix; however, complete copies are available upon request. Table E-3 lists the concentrations of agents predicted to reach the water table, broken out by agent, climate (arid/humid), scenario (remediated/leak), and hydrolysis rate. This concentration is used as the starting concentration in the horizontal-flow model. As mentioned above, the second model generates the time necessary to degrade a given concentration of agent to a specified level (the evaluation endpoint concentration for that agent), then combines this time with ground-water flow velocity to calculate a distance. Figure E-2 presents an example run of the horizontal-flow model. Table E-4 lists the horizontal distances away from the contamination site that ground water will travel before dissolved agent concentrations will fall below evaluation endpoint levels, broken out by agent, climate (arid/humid), scenario (remediated/leak), and hydrolysis rate.

Figure E-2: Example run of the horizontal-flow model

The humid climate, leak scenario of GD lists an actual concentration of 1.69E+1 μg/L reaching ground water (see Table E-3). Table E-1 lists an average hydrolysis half-life for GD of 0.8664 days, and Section H.4.2 lists an evaluation endpoint level of 0.15 μg/L for GD. Therefore:

$$k = -\ln 2 / 0.8664 = -0.80003$$

starting concentration/evaluation endpoint = $(1.69 \times 10^{1}) / 0.15 = 1.13 \times 10^{2}$

$$t = -\ln(1.13 \times 10^{2}) / 0.80003 = 5.91 \text{ days}$$

Then, (5.91 days)(0.13 meters/day) = 0.756 meters

Therefore, when ground water contaminated with the agent GD has traveled approximately 0.76 meters from the point where contamination entered ground water, concentrations of GD will be at or below evaluation endpoint levels.

Table E-3. Maximum concentrations of chemical agent reaching water table
(Unless otherwise noted, maximum concentrations arrived on day one.)

Agent	Scenario	Concentration (μg/L)		
		(Slowest Hydrol. Rate)	(Avg. Hydrol. Rate)	(Fastest Hydrol. Rate)
Arid Climate - deep water table				
HD	remediated[b]	2.45E-51	1.13E-68	1.27E-134
	leak[b]	5.11E-48	2.36E-65	2.65E-131
VX	remediated[b]	9.92E-33	9.26E-33	7.17E-33
	leak[b]	5.84E-30	5.45E-30	4.22E-30
GB	remediated[b]	9.56E-23	1.95E-23	3.61E-37
	leak[b]	1.84E-21	3.75E-22	6.94E-36
GA	remediated[b]	6.99E-25	5.87E-26	1.20E-27
	leak[b]	8.13E-24	6.83E-25	1.40E-26
GD	remediated[b]	1.76E-25	1.04E-25	2.18E-33
	leak[b]	1.69E-23	1.00E-23	2.10E-31
L[a]	remediated[b]	4.33E-25	2.83E-79	<1E-300
	leak[b]	1.27E-24	8.31E-79	<1E-300
Humid Climate - shallow water table				
HD	remediated[b]	3.80E-30	1.75E-47	1.97E-113
	leak[b]	7.91E-27	3.65E-44	4.10E-110
VX	remediated[b]	5.27E-6	4.92E-6	3.81E-6
	leak[b]	3.10E-3	2.89E-3	2.24E-3
GB	remediated[b]	1.64E-2	3.34E-3	6.18E-17
	leak[b]	3.14E0	6.42E-1	1.19E-14
GA	remediated[b]	9.38E-3	7.87E-4	1.62E-5
	leak[b]	1.09E-1	9.15E-3	1.88E-4
GD	remediated[b]	3.23E-2	1.92E-2	4.01E-10
	leak[b]	3.11E0	1.84E0	3.85E-8
L[a]	remediated[b]	1.73E-3	1.13E-57	<1E-300
	leak[b]	5.10E-3	3.33E-57	<1E-300
Arid Climate - shallow water table				
HD	remediated[b]	1.01E-28	4.66E-46	5.24E-112
	leak[b]	2.10E-25	9.70E-43	1.09E-108
VX	remediated[b]	2.22E-4	2.07E-4	1.60E-4
	leak[b]	1.30E-1	1.22E-1	9.43E-2
GB	remediated[b]	3.05E0	6.23E-1	1.15E-14
	leak[b]	5.87E+1	1.20E+1	2.22E-13
GA	remediated[b]	1.91E-1	1.60E-2	3.29E-4
	leak[b]	2.22E0	1.86E-1	3.82E-3
GD	remediated[b]	1.07E0	6.32E-1	1.32E-8
	leak[b]	1.03E+2	6.08E+1	1.27E-6
L[a]	remediated[b]	1.78E-2	1.16E-56	<1E-300
	leak[b]	5.25E-2	3.42E-56	<1E-300

a Values for Lewisite may be extreme overestimates as discussed in text.

b See section E.3 - SCENARIO CHARACTERIZATIONS for definitions of the "remediated" and "leak" scenarios.

Table E-4. Predictions of ground-water flow before complete hydrolysis[a] of chemical agent

Agent	Scenario	Horizontal distance (m) from site of contamination		
		(Slowest Hydrol. Rate)	(Avg. Hydrol. Rate)	(Fastest Hydrol. Rate)
Arid Climate - deep water table				
HD	remediated[b]	0	0	0
	leak[b]	0	0	0
VX	remediated[b]	0	0	0
	leak[b]	0	0	0
GB	remediated[b]	0	0	0
	leak[b]	0	0	0
GA	remediated[b]	0	0	0
	leak[b]	0	0	0
GD	remediated[b]	0	0	0
	leak[b]	0	0	0
L	remediated[b]	0	0	0
	leak[b]	0	0	0
Humid Climate - shallow water table				
HD	remediated[b]	0	0	0
	leak[b]	0	0	0
VX	remediated[b]	0	0	0
	leak[b]	0	0	0
GB	remediated[b]	0	0	0
	leak[b]	2.9	0	0
GA	remediated[b]	0	0	0
	leak[b]	0	0	0
GD	remediated[b]	0	0	0
	leak[b]	1.4	0.4	0
L	remediated[b]	0	0	0
	leak[b]	0	0	0
Arid Climate - shallow water table[c]				
HD	remediated[b]	0	0	0
	leak[b]	0	0	0
VX	remediated[b]	0	0	0
	leak[b]	260.6	27.0	5.3
GB	remediated[b]	26.2	0	0
	leak[b]	80.4	2.1	0
GA	remediated[b]	0	0	0
	leak[b]	0.2	0	0
GD	remediated[b]	8.6	2.2	0
	leak[b]	28.7	9.2	0
L	remediated[b]	0	0	0
	leak[b]	0	0	0

a "Complete hydrolysis" defined as the evaluation endpoint levels calculated in section H.4.

b See section E.3 - SCENARIO CHARACTERIZATIONS for definitions of the "remediated" and "leak" scenarios.

c Original ground-water flow rate (1.22 m/day) used. Altered flow rate (0.13 m/day) used in Table E-5.

The arid climate was further altered to reflect both the water table depth and ground-water flow rates of the humid climate, so that comparisons could be made. Table E-5 shows this comparison. The slight differences- 1.4 m (humid) vs. 3.1 m (arid) found in the GD "leak" scenario for example- may be due to the greater soil organic carbon content found in the humid soil. With more organic carbon on which to adsorb, less agent will travel.

Table E-5. Comparison of humid and arid climates with the same depth to water table and ground-water flow rate

Distances ground water travels before chemicals hydrolyze to below evaluation endpoint levels

Agent	Scenario	Horizontal distance (m) from site of contamination					
		(Slowest Hydrol. Rate)		(Avg. Hydrol. Rate)		(Fastest Hydrol. Rate)	
		Humid	Arid	Humid	Arid	Humid	Arid
HD	remediated[a]	0	0	0	0	0	0
	leak[a]	0	0	0	0	0	0
VX	remediated[a]	0	0	0	0	0	0
	leak[a]	0	27.8	0	2.9	0	0.6
GB	remediated[a]	0	2.8	0	0	0	0
	leak[a]	2.9	8.6	0	0.2	0	0
GA	remediated[a]	0	0	0	0	0	0
	leak[a]	0	0	0	0	0	0
GD	remediated[a]	0	0.9	0	0.2	0	0
	leak[a]	1.4	3.1	0.4	1.0	0	0
L[a]	remediated[a]	0	0	0	0	0	0
	leak[a]	0	0	0	0	0	0

a See section E.3 - SCENARIO CHARACTERIZATIONS for definitions of the "remediated" and "leak" scenarios.

To further investigate the potential of both soil carbon and depth to water table to effect final output, additional runs of the models were performed using the agent VX/arid/leak combination. Table E-6 shows the outcomes, detailing parameter values used and the horizontal distance traveled by aqueous agent before hydrolyzing to below evaluation endpoint levels. According to these models, VX is clearly highly sensitive to organic carbon content in the soil. This is not surprising, considering VX has the highest K_{oc} (i.e., the highest affinity to organic carbon) of any of the agents modeled. It is also clear that the vertical distance these compounds must travel before reaching ground water has a substantial effect.

Table E-6. Effects of soil carbon and water table depth on horizontal distance traveled

Agent VX, arid climate, leak scenario, 1.22 m/day flow rate, slowest hydrol. rate

Organic Carbon Content	Depth to Water Table (m)	Horiz. Distance Traveled (m)
0.001*	3.7*	260.6*
0.002	3.7	170.2
0.003	3.7	114.4
0.0035	3.7	93.1
0.001	4.9 (16 feet)	47.0
0.002	4.3 (14 feet)	63.4

* from Table E-4

E.6 DISCUSSION AND CONCLUSIONS

The following points were considered during the development and use of these models:

- Karst and macropore formations - Vadose water and ground water can be modeled in karsts and macropore formations, but only with great difficulty and uncertainty. The models used in this appendix do not apply to karsts and macropores.
- Multiple soil types - It is reasonable (and only practical, without investment of much more effort) to assume that there is a single soil type of moderately high hydraulic conductivity rather than attempting to estimate the combined effects of bands of different soil types having different thicknesses. Such an assumption is likely to lead to an overestimation of the rate at which substances pass through the vadose zone. Also, a single-soil value is more "generic" than a multi-soil value. It should be understood that the values generated for this appendix are only valid for homogeneous subsurface conditions.
- Diffusion - An assumption that there is no diffusion adds conservatism to the outcome by increasing agent concentration.
- Evapotranspiration - An assumption that there is no evapotranspiration adds conservatism by increasing the volume of agent reaching ground water.
- Soil pH - Chemical agent hydrolysis rates are often highly pH dependent (see Table 1-1), but disagreement is found in the literature. Some of the slowest and fastest hydrolysis rates considered occur at pH's unlikely to be encountered in nature. Further research should be conducted into the correlation between soil pH and chemical agent hydrolysis rates.

Choices regarding models and parameter values used, and assumptions made, among other choices, were influenced by the intent to generate estimates of concentration and distance that would be reasonably, but not overly, conservative. The intent was not to characterize an actual scenario as completely as possible, but rather to calculate worst-case values for a range of possible sites/scenarios, which actual values would be unlikely to exceed.

As noted above, horizontal distances required to reach evaluation endpoint levels are zero for the great majority of all scenarios. In most cases, dissolved chemical agent migrating vertically through the vadose zone hydrolyzes to below endpoint levels before ever reaching ground water. Of those predicted to have some horizontal flow, only one shows a distance over 100 meters. Considering the level of conservatism incorporated in the modeling, the results tend to support the view that the chemical agents modeled are not likely to contaminate ground water. Future modeling efforts should consider the following:

- Particularly in situations of limited precipitation (e.g., arid climates or drought conditions), evapotranspiration is an important parameter to include in fully characterizing potential groundwater contamination. A percentage of precipitation will evaporate from the surface or be transpired by local plant life. This percentage is then no longer available to transport chemical agent to the water table. At the extreme at which all precipitation evapotranspirates, there is none available for agent transport. In effect, the pathway is broken before the agent reaches groundwater and, hence, the agent does not pose a threat to receptors via ground water. This is not an unreasonable scenario: In the Tooele region of Utah, for instance, local precipitation does not contribute to groundwater; all recharge comes from the surrounding mountains. Since there has been no opportunity yet to explicitly model evapotranspiration, this is one area in which additional modeling could reduce the level of uncertainty associated with model output.

- Geologic and hydrologic conditions such as soil type, depth to water table, and hydraulic conductivity can vary widely at any individual site. This makes developing "generic" distance-from-site numbers of any sort difficult and "universal" numbers (equally valid in any scenario) unlikely. Also, failure to fully characterize site-specific hydrogeology for any site increases the uncertainty associated with model output.

- Perhaps due to their military-unique nature, comparatively little research has been performed on these chemical agents, as opposed to hazardous chemicals used in industry. There is considerable disagreement in the literature on a number of chemical-specific parameters (as the range of values for hydrolysis rates will attest), and there are still many data gaps (hydrolysis and K_{oc} values for Lewisite, for example). Larger data gaps exist regarding the fate and transport of chemical agents in the environment. Available hydrolysis rates for agents are based on pure agent dissolved in various volumes of unbuffered water, rather than agent found in soil, where the available data suggest hydrolysis is considerably faster.

- Even less is known about the degradation products of chemical agents (see Appendix F). Several of these products, particularly EA-2192 and Lewisite oxide/chlorvinyl arsonous acid (CVAA), are estimated to be somewhat more environmentally stable than the source agents, while are assumed to retain significant toxic properties. Since this particular assessment does not address the potential for these breakdown /degradation products to migrate via groundwater, further research to determine the environmental parameters for these compounds, as well as modeling their potential for ground-water contamination, may be warranted.

- Model calibration (i.e., multiple runs during which variable parameters are altered until output consistently matches empirical evidence) is a vital step in ensuring that any predictions made by the model can be considered valid. Unfortunately, a very limited database was available to calibrate these models[2]. In addition to the fate and transport research mentioned above, additional research is needed to develop empirical evidence against which future modeling can be verified.

References:

James M. Montgomery, Consulting Engineers, Inc. (1987). Ground-Water Quality Assessment Engineering Report, Tooele Army Depot, Utah. Salt-Lake City, Utah.

Ravi, V. and J.A. Johnson (1996). VLEACH- a one dimensional finite difference vadose zone leaching model. Version 2.0. With supplement for Version 2.2a. Publication of Dynamic Corporation available at http://earth1.epa.gov/ada/models.html.

Rosenbloom, J., P. Mock, P. Lawson, J. Brown, and H.J. Turin. (1993) Application of VLEACH to Vadose Zone Transport of VOCs at an Arizona Superfund Site. Ground Water Monitoring and Remediation 13: 159-169.

Small, M. J. (1984). Compounds Formed From the Chemical Decontamination of HD, GB, and VX and Their Environmental Fate. U.S. Army Medical Bioengineering Research & Development Laboratory. Fort Detrick, Frederick, Maryland. AD A149515.

State of Utah, Department of Natural Resources (1981). Information Bulletin No. 26: Test Drilling For Fresh Water in Tooele Valley, Utah.

U.S. Geological Survey (1996). Water-Resources Investigations Report 95-4248: Hydrologic Setting, Hydraulic Properties, and Ground-water Flow at the O-field Area of Aberdeen Proving Ground, Maryland.

[2] Other reports regarding the USGS study of New O-field at the Edgewood Area of APG reported that no chemical agents that were tested for were found in ground water, which agrees with predictions made using the models discussed in this appendix.

APPENDIX F

PRIMARY BREAKDOWN PRODUCTS OF CHEMICAL AGENTS

The breakdown products of the chemical agents discussed in this report that are considered to be relatively persistent in the environment and/or potentially toxic are listed in Table F-1. These compounds were identified through an assessment of various breakdown products formed through different processes (Munro et al., submitted for publication, Dec 1998).

Table F-1. Primary chemical agent degradation products of potential concern in the environment

Agent	Degradation Product	Formula	CAS No.	Chronic Toxicity Values[a]
Sulfur Mustard (HD)	Thiodiglycol (TDG)	$C_4H_{10}SO_4$	111-48-8	RfD_o = 0.17 mg/kg/day[b]
Tabun (GA)	*None of potential concern*	-	-	-
Sarin (GB)	Methyl phosphonic acid (MPA)	CH_5PO_3	993-13-5	RfD_o = 0.02 mg/kg/day[b]
	Isopropyl methylphosphonic acid (IMPA)	$C_4H_{11}PO_3$	1832-54-8	RfD_o=0.10 mg/kg/day
Soman (GD)	Methyl phosphonic acid (MPA)	CH_5PO_3	993-13-5	RfD_o = 0.02 mg/kg/day[b]
Agent VX	*S*-(Diisopropylaminoethyl) methylphosphonothioate (EA-2192)	$C_9H_{22}NSPO_2$	73207-98-4	RfD_o = 6 x 10^{-7} mg/kg/day[e]
	Ethyl methylphosphonic acid (EMPA)	$C_3H_9PO_3$	1832-53-7	RfD_o = 0.028 mg/kg/day[c]
	Methyl phosphonic acid (MPA)	CH_5PO_3	993-13-5	RfD_o = 0.02 mg/kg/day[b]
Lewisite	2-chlorovinyl arsonous acid (CVAA)[h]	$C_2H_4AsClO_2$	85090-33-1	RfD_o = 0.0001 mg/kg/day[f]
	Lewisite oxide (Chlorovinyl arsenous oxide[g])	C_2H_2ClAsO	3088-37-7	RfD_o = 0.0001 mg/kg/day[f]
	Vinyl chloride	C_2H_3Cl	75-01-4	-
	Inorganic arsenic [i]	As	7440-38-2	RfD_o = 0.3 µg/kg/day[d]; oral SF^d = 1.5 $(mg/kg/day)^{-1}$; inhalation unit risk[d] = 0.0043 per µg/m^3

[a] Toxicity values developed by USACHPPM (see Annex F.1) unless otherwise indicated

[b] QSAR estimate.

[c] Based on similar toxic properties of the related compound isopropyl methyl phosphonic acid (RfD = 0.2 mg/kg; EPA, 1997a)

[d] EPA 1997a, *Integrated Risk Information System (IRIS).* Online file.

[e] RfD is the same as that used for VX

[f] RfD is the same as that used for Lewisite

[g] Also referred to as Lewisite oxide, is a dehydration product of Lewisite; it is assumed that in most ambient environments Lewisite oxide would immediately replace its parent compound

[h] 2-chlorovinyl arsonous acid (CVAA) is more likely to be found in aqueous matrices than Lewisite or Lewisite oxide. However, since CVAA is of limited persistence and in many cases has limited solubility, it may not be a significant concern for contamination of aqueous media such as groundwater. Instead, inorganic arsenic should be evaluated in cases where Lewisite contamination is suspected.

[i] As arsenic is ubiquitous in the environment and may be present in significant concentrations from sources having no relationship to agent, evaluations of arsenic must be done with adequate data on background arsenic concentrations. See text.

The compounds in Table F-1 may be useful as "indicators" of past chemical agent presence but, in addition, there may be some questions as to the potential health risks associated with these breakdown/ degradation products in certain environmental scenarios. The risk assessment methodologies described throughout this report can be used to determine Health Based Environmental Screening Levels (HBESLs) for some of the potential toxic compounds. The risk assessment algorithms require the input of chronic toxicity values (e.g., RfD_os and for noncarcinogens and CSF_os for carcinogens). The USEPA approved chronic toxicity values are available for only a few of these compounds. Where EPA values were not available, they were estimated by USACHPPM using Quantitative Structure-Activity Relationships (QSAR) methods or by comparison with structurally related compounds (see Table F-1 and also Annex F.1). These toxicity values have not yet been verified by EPA. The values presented are based on currently available data with certain extrapolations or assumptions, and are only presented as suggested values pending further study and review. For those breakdown compounds deemed of significant toxicity, example screening levels have been calculated using methods and described previously in this document.

The information below summarizes the basis for selected the identified compounds in Table F-1 as described in Munro et al, submitted for review, December 1998. Toxicity estimates are based on the derivations described in Annex F.1

Agent HD. When dissolved in water agent HD hydrolyzes rapidly to thiodiglycol. Thiodiglycol (TDG) has a high RfD (0.17 mg/kg/day), indicating that it is relatively nontoxic; therefore, HBESLs have not been calculated for it. Its presence in soil or water can be used as an indicator of past contamination with agent HD, although it is not unique to HD degradation due to the possible commercial application of thiodiglycol in the manufacture of soap products and polymers. Other, secondary degradation products may be found in certain soil types. In particular, the compound thiodiglyotic acid (TDGA) may occur through a biological transformation of TDG, though this may not occur in all soil types.

Agent GA. As described previously in this document (Section 1.2.3),Agent GA is not persistent in the environment. Literature reviews have not established any environmentally persistent or toxic degradation products that would be associated with this agent.

Agent GB. Methyl phosphonic acid (MPA) is the primary breakdown product of agent GB. The estimated oral RfD is 0.02 mg/kg/day, indicating that it is relatively nontoxic; therefore, HBESLs were not calculated. A secondary breakdown product of Agent GB is isopropyl methylphosphonic acid (IMPA), with an estimated RfD of 0.1 mg/kg/day (relatively nontoxic). As a consequence, no HBESLs were calculated for this compound.

Agent GD. Methyl phosphonic acid (MPA) is the primary breakdown product of agent GD. The estimated oral RfD is 0.02 mg/kg/day, indicating that it is relatively nontoxic; therefore, HBESLs were not calculated.

Agent VX. Agent VX has three primary breakdown products, EA-2192, ethyl methylphosphonic acid (EMPA) and methyl phosphonic acid (MPA). EA-2192 has an estimated vapor pressure of 5.24×10^{-6} mm Hg, an estimated water solubility of 1.4×10^{4} mg/L at 25 °C, an estimated K_{ow} of 1.52, and an estimated Henry's Law Constant of 4.38×10^{-12} atm-m^3/mol (Howard and Meylan, 1997). According to the USEPA, compounds with Henry's Law Constants less than 1×10^{-5} atm-m^3/mol are not likely to pose an inhalation hazard as a result of volatilization from water or soil. Because of its relatively high water solubility, EA-2192 is a potential contaminant of groundwater. The estimated oral RfD for EA-2192 was set at the same value as the RfD for VX (see Annex F.1). This is believed to be an extremely conservative approach because EA-2192 exists in an ionized state which would reduce absorption through the gastrointestinal tract. In addition, acute oral and dermal toxicity data indicate that EA-2192 is somewhat less toxic than VX by these pathways (see Annex F.2). However, given the paucity of data and various uncertainties, the conservative approach is suggested. HBESLs for EA-2192 are listed in Table F-2.

The estimated oral RfD for EMPA is 0.03 mg/kg/day and that for MPA is 0.02 mg/kg/day. Therefore, both of these breakdown products are considered to be relatively nontoxic and HBESLs were not calculated for them.

Lewisite. In aqueous media, Lewisite hydrolyzes to 2-chlorovinyl arsonous acid (CVAA). In an aqueous solution (to include soil with significant moisture) the primary Lewisite degradation product present expected is 2-chlorovinyl arsonous acid; Lewisite oxide (also referred to as chlorovinyl arsenous oxide or chlorovinyl arsenoxide) occurs only as a dehydration reaction products and therefore maybe expected in drier media. Given the limited data available, CVAA and Lewisite oxide are currently considered to be as toxic as Lewisite itself. HBESLs for 2-chlorovinyl arsonous acid/Lewisite oxide are listed in Table F.2. However, it should be noted that both CVAA/Lewisite oxide will further degrade resulting in the formation of vinyl chloride and inorganic arsenic. *These compounds, particularly inorganic arsenic, should be considered the primary constituent of concern when evaluating environmental media for potential Lewisite contamination - its is particularly unlikely that the other compounds would persist long enough to present a chronic health risk.*

It is important to realize, however, that in evaluating sites for arsenic contamination as a potential result from Lewisite degradation, consideration must be given to naturally occurring background levels of arsenic - arsenic is ubiquitous in environmental media and in many geographic areas may be found in concentrations greatly exceeding health/risk - based screening levels. Specifically, national background concentrations range from about 1 - 40 ppm, with a mean value of about 5 ppm; however, soils overlying arsenic rich ores may have concentrations two orders of magnitude higher. In addition, industry (e.g. smelter operation) and agricultural applications (pesticides/herbicides) may retain substantial amounts of arsenic (ATSDR, 1993). In addition, the valence state of the arsenic present at a site must be determined. This is important because the toxicity of inorganic arsenic varies with valence state, with the trivalent form being much more toxic than the pentavalent form. Environmental screening levels (e.g. PRGs) for vinyl chloride and inorganic arsenic are available from EPA Region IX (USEPA, 1996b/1998) and are therefore not calculated in this document but should be considered when evaluating media/sites for Lewisite contamination.

Table F-2. Summary of calculated HBESLs for key agent breakdown products

	Residential soil (mg/kg)			Industrial soil (mg/kg)		
	RBCs	PRGs	SSLs	RBCs	PRGs	SSLs
EA-2192 [a]	0.047	0.042	0.047	1.2	1.1	NA
2-Chlorovinyl-arsonous acid/Lewisite oxide [b]	7.8	0.3	7.8	(7.8)[c]	3.7	NA

[a] Based on VX toxicity; parallels VX screening levels

[b] These values are based on Lewisite toxicity; In addition, vinyl chloride and arsenic should be evaluated during site assessments. The existing USEPA screening levels for these two compounds should be consulted.

[c] As with Lewisite calculations, RBC value derived for the commercial/industrial scenario was potentially above acute toxicity levels, therefore the upper bound value of the residential scenario is suggested as a substitute. See Section 9.1 of this document.

Summary. When evaluating chemical agent contamination in environmental media, it is necessary to realize that under many if not most circumstances, the agent will breakdown/degrade in relatively short amounts of time. While analyses may not show the presence of agent, there may be a need to determine previous presence of agent or, in certain circumstances, there may be a breakdown product that itself poses a potential health risk of concern. Though there are numerous breakdown products, only a few are substantially persistent in the environment and even fewer that are of significant toxicity. Specifically, the products EA-2192 (from VX) and CVAA and Lewisite oxide from Lewisite are potential health concerns and may need to be evaluated against HBESLs or through a site-specific health risk assessment. Also, inorganic arsenic should be evaluated at sites involving Lewisite, though care must be given to proper evaluation of naturally occurring/anthropogenic background concentrations of arsenic (this compound is currently regulated and there are existing EPA screening levels). Other persistent compounds of relatively insignificant toxicity include TDG (from HD), and MPA and EMPA (from VX and GB and GD) which may be useful in tracing previous agent presence or sources. Finally, the assessor should be aware of other potential contaminants associated with the source of chemical agent such as chloroform from Chemical Agent Identification Sets (CAIS) for which there are also existing EPA screening levels.

APPENDIX F - ANNEX F.1

MCHB-TS-THE 10 December 1998

MEMORANDUM FOR: Veronique Hauschild, Chemical Agent Systems Working Group, USACHPPM, Aberdeen Proving Ground, MD 21010

SUBJECT: Report on Suggested RfD and RfC for Selected Agent-Related Compounds

1. Attached is a report entitled "Suggested Interim Estimates of the Reference Dose (RfD) and Reference Concentration (RfC) for Certain Key Breakdown Products of Chemical Agents"

2. These estimates are only interim in nature and are intended to assist with risk assessments of chemical agent contaminated sites. The compounds dealt with may have to be sampled for in soil, water or air for purposes of human health and ecological risk assessment. The estimates will be of use in making cleanup decisions regarding polluted sites or following spill events. They will also be of use in developing safe processes for demilitarization/detoxification of agents and agent-containing munitions.

3. In developing the estimates, existing values for the RfD were first ascertained. If there were none, proposed RfDs, developed from experimentally-determined NOAELs or LOAELs were considered. If there were none, then a RfD estimate was estimated using (1) a NOAEL or LOAEL determined for a structurally-related compound or (2) a rat chronic LOAEL estimated by Quantitative Structure-Activity Relationships (QSAR). The QSAR system used was the TOPKAT ® system (Health Designs, Inc., Rochester, NY). (Enslein, K. Pharm. Rev. 36 (2): 131S-135S, 1984.

4. The suggested interim values are submitted for comment to the Working Group and also to selected individuals in the USEPA.

5. POC for this action are Howard T. Bausum, 410-436-5063, and the undersigned, 410-436-3980.

Glenn J. Leach
Program Manager
Health Effects Research
USACHPPM

SUGGESTED INTERIM ESTIMATES OF THE REFERENCE DOSE (RfD) AND REFERENCE CONCENTRATION (RfC) FOR CERTAIN KEY BREAKDOWN PRODUCTS OF CHEMICAL AGENTS

Report to the USACHPPM Chemical Standards Working Group

10 December 1998

Howard T. Bausum, Gunda Reddy and Glenn J. Leach
Health Effects Research Program, Directorate of Toxicology
U.S. Army Center for Health Promotion and Preventive Medicine

Suggested Interim Estimates of the Reference Dose (RfD) and Reference Concentration (RfC) for Certain Key Breakdown Products of Chemical Agents

to the USACHPPM Chemical Standards Working Group

Introduction

There is a need for estimates of the oral Reference Dose (RfD) for certain chemical agent products. The compounds of interest are key environmental breakdown products, associated with chemical agents, which may have to be sampled for in soil and water for purposes of human health and ecological risk assessment. Estimates of the RfD will be of use in making decisions regarding cleanup levels for polluted sites or following any unexpected spill event, and in developing detoxification processes for agents and agent-containing munitions. The present agent demilitarization program has heightened the need for such information.

In this report we seek to identify the best estimate of the RfD for the following important and prevalent breakdown products: thiodiglycol (TDG), methyl phosphonic acid (MPA), ethyl methyl phosphonic acid (EMPA), EA2192, and Lewisite oxide, taken together with its hydrated form, 2-chlorovinyl arsonous acid (CVAA). Some basic information about each of these, including the molecular structure and the chemical agent with which it is associated, is given in Table 1. Carcinogenicity is not considered to be a likely problem with any of these, although there is little information on this at present.

The toxicology database on most of these substances is quite limited. This has required conservative or safe-sided estimates, leading in some cases to reasoning from a structurally-related compound, and in others to estimation of RfD based on Quantitative Structure-Activity Relationships (QSAR).

Methods used by the USEPA for derivation of inhalation Reference Concentrations (RfCs) are similar in concept to those used for oral RfDs. Although RfC is a concentration, while RfD is a dose level, both are derived from NOAELs by applying uncertainty factors. The actual analysis of inhalation exposure is, however, more complex than that for oral exposure. In this report suggested RfCs are derived by direct calculation from the suggested RfD and are intended to serve as screening levels only.

Methods

In suggesting the best possible estimate of RfD for each compound, a chronic or subchronic NOAEL or LOAEL is given first preference, the RfD being then developed using an uncertainty factor (UF) chosen according to USEPA criteria. An experimentally determined chronic or subchronic NOAEL or LOAEL was not found for any of the compounds dealt with in this report, except for TDG.

If a NOAEL or LOAEL is not available, an estimate of the rat chronic LOAEL, derived from Quantitative Structure-Activity Relationships (QSAR) was the next choice. This was done for TDG and MPA, using the commercially-available software system TOPKAT ® (reference 1). In this case a UF was also developed, following USEPA criteria where possible.

For some compounds neither an experimentally determined value nor a QSAR estimate for subchronic or chronic toxicity was available. In these cases, a RfD was derived using data from a structurally related compound of comparable toxicity. Thus, in the case of EMPA, a RfD estimate was derived using an experimentally-derived rat subchronic NOAEL for isopropyl methylphosphonic acid (IMPA). Similarly, an estimate for lewisite oxide was made using an experimental rat subchronic NOAEL value for Lewisite, while LOAEL values for VX were used as surrogates for the related structure EA2192.

Suggested RfCs were derived by calculation from the calculated RfDs as described above. Where RfC were not available from either the Integrated Risk Information System (IRIS, USEPA) or the Health Effects Assessment Summary Tables (HEAST, USEPA) the RfC values were derived by multiplying the suggested chronic oral RfD (in mg/kg/day) by 70 kg (average body weight of an adult), then dividing by 20 m^3/day (average adult inhalation rate) and finally multiplying by 1000 to derive a value in microgram/m^3 (references 2,3,4). Thus we employed the following equation to extrapolate oral RfDs to RfCs.

$$RfC = \frac{RfD \times 70\,kg}{20\,m^3 \times UF} \times 1000$$

where:
RfC- Inhalation Reference Concentration, micrograms/m^3
RfD- Reference Dose, mg/kg/day
70kg- Average body weight of an adult, kilograms
20m^3- Average adult inhalation rate, meter ^{3}
UF- Uncertainty Factor of three {3} to allow for the uncertainty of extrapolation from an oral to an inhalation route of exposure

Development of Reference Dose

Thiodiglycol: For this substance an oral LD_{50} of 6610 mg/kg was determined in rats (reference 5), indicating rather low toxicity. Estimates using TOPKAT QSAR included 2700 mg/kg for rat oral LD_{50}, in fair agreement with the experimental figure (reference 6). The QSAR estimate for rat chronic LOAEL is 1700 mg/kg/day. No evidence for carcinogenicity was found, and the QSAR estimate for this was negative in all of three rodent models.

One provisional estimate of the RfD can be made by use of the QSAR-estimated LOAEL, 1700 mg/kg/day. The safety factor to be applied, i.e., the Uncertainty Factor (UF), should allow a factor of ten for extrapolation from animal study to man, a factor of ten to provide for variation in sensitivity within human populations, a factor of ten for use of a LOAEL instead of NOAEL, and at least a factor of three for use of a QSAR estimate as opposed to experimental data. The UF is then developed as follows:

UF1	=	10	(Extrapolation from an animal study to man (interspecies))
UF2	=	10	(Human (intraspecies) variability (sensitive subpopulations))
UF3	=	10	(Extrapolation from LOAEL to NOAEL)
UF4	=	3	(Database uncertainties: lack of reproductive and genotoxicity studies)

The uncertainty factor is then:

UF = 10 x 10 x 10x 3 = 3,000

The estimate is also adjusted by use of a Modifying Factor (MF) which in this case allows for the use of a QSAR prediction as a basis for RfD derivation. A MF of 3 is assigned.

MF = 3

The RfD is derived according to the equation:

$$RfD = \frac{LOAEL}{UF \times MF} = \frac{1700\ mg/kg/da}{3000 \times 3} = 0.17\ mg/kg/day = 170\ ug/kg/day$$

All RfD estimates, together with essential information about their derivation, are summarized in Table 2.

An alternative estimate of the RfD for this compound can be derived from our ongoing toxicity evaluation of TDG in rats. A 14-day study was conducted in which neat TDG was administered by oral gavage to male and female rats (six/group/sex) at doses of 0, 157, 313, 625, 1250, 2500, and 5000 mg/kg BW/day (5 days/week) (reference 7). No clinical signs or gross morphological changes were noticed in either sex. At the highest dose level, changes in food consumption, and body and kidney weights were observed. Some clinical chemistry parameters were affected at the two highest doses, 2500 and 5000 mg/kg/day. A drop in WBC was seen at higher doses (1250 and 2500) but not at the highest dose, 5000 mg/kg/day.

The 1250 mg/kg/day level was determined to be a NOAEL level. This is suggested by the absence of clinical chemistry, body weight, or organ weight changes, and that the one hematological effect, lowered WBC, was not dose dependent. Histopathology information was not included, but effects at 1250 mg/kg/day are considered unlikely in the light of the body and organ weight results.

The UF is developed as follows:

UF1 = 10 (Use of an animal study)
UF2 = 10 (Human variability)
UF3 = 3 (Database uncertainties: lack of developmental and reproductive studies)
UF4 = 10 (Extrapolation from subchronic to chronic)

The Uncertainty Factor is then:

UF = 10 x 10 x 3 x 10 = 3,000

Modifying Factor (for extrapolation from 14 day to subchronic study)

MF = 3

The RfD estimate is then:

$$RfD = \frac{1250\ mg/kg/day}{3,000 \times 3} = 0.13\ mg/kg/day = 130\ ug/kg/day$$

Thus the RfD, as determined on the basis of the NOAEL from a 14- day study agrees quite well with the value derived from the QSAR estimate of the rat chronic LOAEL: 130 ug/kg/day compared to 170 ug/kg/day.

Preferred Derivation:

In a recent subchronic study (rat, 90 day), a NOAEL of 500 mg/ kg/ day was determined (reference 7). This value, because it is based on an experimental result from a subchronic test, will be used here. The MF of 3 for extrapolation from 14 day to subchronic duration is therefore dispensed with.

$$RfD = \frac{500 \text{ mg/ kg/ day}}{3{,}000} = 0.17 \text{ mg/kg/day} = 170 \text{ ug/kg/day}$$

Methylphosphonic Acid: The three compounds MPA, IMPA, and diisopropyl methylphosphonic acid (DIMP) seem to be of very similar toxicity. Thus, for IMPA, the rat subchronic NOAEL was experimentally determined to be 279 mg/kg/day (reference 8), while the rat chronic LOAEL was estimated by TOPKAT to be 221 mg/kg/day (6). For DIMP the rat LD_{50} was experimentally determined to be 826 mg/kg (9). A LOAEL of 330 mg/kg/day and NOAEL of 56.5 mg/kg/day were determined for DIMP using mink as the experimental animal (reference 10). For MPA, an experimental LD_{50} of 5000 mg/kg was reported (reference 11). The TOPKAT estimate for rat chronic LOAEL is 566 mg/kg/day. Experimental values for this were not found; therefore in this report the QSAR estimate for rat chronic LOAEL will be used.

QSAR estimate of rat chronic LOAEL = 566 mg/kg/day

The UF is derived as follows.

UF1 = 10 (Extrapolation from an animal study)
UF2 = 10 (Individual/ subgroup variation)
UF3 = 10 (Extrapolation from LOAEL to NOAEL)
UF4 = 3 (Use of a QSAR estimate)

The Uncertainty Factor is then:

UF = 10 x 10 x 10 x 3 = 3000

MF, incomplete data base = 3

The RfD is then:

$$RfD = \frac{566 \text{ mg/kg/day}}{3000 \text{ x3}} = 0.057 \text{ mg/kg/day} = 57 \text{ ug/kg/day}$$

Preferred Derivation:

A provisional RfD for MPA has been suggested in a USEPA issue paper (reference 12), in which the RfD is derived from analogy to isopropyl methylphosphonic acid (IMPA). For this compound, an experimentally determined subchronic NOAEL in the rat has been determined. This, and a RfD value (100ug/kg/da) derived from it using a UF of 3000, have been placed in the USEPA's IRIS database (reference 13). The RfD value suggested for MPA (reference 12) is based on a total UF of 10,000 and includes an adjustment factor for the ratio of th emolecular weight of MPA to that of IMPA. The suggested RfD value for MPA is then 0.02 mg/kg/day (=20 mg/kg/day).

Ethyl Methylphosphonic Acid and Isopropyl methylphosphonic acid: The only EMPA data point available is a QSAR estimate of 65 mg/kg for the rat oral LD_{50} (reference 6). This suggests a toxicity somewhat greater than that of MPA, but there is no confirmation of this. The approach taken in developing a provisional RfD for EMPA is to use data from the structurally related compound IMPA, for which a RfD has been developed and placed in

USEPA's IRIS database (reference 13). In this approach the experimentally-determined subchronic NOAEL (rat) for IMPA, 279 mg/kg/day (reference 8), is used. The UF is derived thus:

For **IMPA**:

UF1 = 10 (Extrapolation from animal study to man)
UF2 = 10 (Allowing for sensitive individuals)
UF3 = 10 (Subchronic study to chronic)
UF4 = 3 (Lack of reproductive or developmental toxicology study or tox study in second species)

The Uncertainty Factor is then:

$$UF = 10 \times 10 \times 10 \times 3 = 3{,}000$$

The Modifying Factor is:

$$MF = 1$$

$$RfD = \frac{279 \text{ mg/kg/da}}{3000 \times 1} = 0.1 \text{ mg/kg/da} = 100 \text{ ug/kg/da}$$

For **EMPA**:

An additional uncertainty factor of 3 is applied for use of a structurally related compound

$$RfD = \frac{0.1 \text{ mg/kg/da}}{3} = 0.028 \text{ mg/kg/da} = 28 \text{ ug/kg/day}$$

This value introduces the uncertainty of reasoning from a structurally-related compound. However, limited information suggests that IMPA and EMPA are quite similar in toxicity. The estimate is probably reliable, especially in view of the large UF employed in its derivation.

EA 2192: There are scant toxicology data on this compound, though a dermal study in rabbits suggests an acute toxicity only somewhat less than that of the parent VX, perhaps less than an order of magnitude (reference 14). Studies of toxicity changes during hydrolysis of VX show a decrease in toxicity (cholinesterase inhibition), but the fall in toxicity does not keep pace with the disappearance of VX. This indicates that the toxic hydrolysis product EA2192 possesses a toxicity that is lower, but comparable, to that of the parent VX (reference 15). Toxicity estimates using the TOPKAT QSAR system gave unreliable results (reference 6), and these cannot be used in estimation of a RfD.

Because of the similarity to VX, as well as the lack of useful data or useful QSAR estimates, the experimental toxicity values available for VX will be used as a surrogate for EA2192. In deriving an estimate of the RfD for the related EA2192, a factor of ten for use of a related compound will not be necessary, because VX is considered to be at least as toxic as EA2192.

There is currently no RfD for VX published in the IRIS database. An interim RfD has been published by the Army Surgeon's Office and is currently being reviewed by the National Academy of Sciences/ NRC SubCommittee on Chronic Reference Doses for Selected Chemical Warfare Agents (reference 16). The interim RfD is 0.0006 ug/kg/day, and was derived from a LOAEL of 0.06 ug/kg/day determined on the basis of whole blood cholinesterase inhibition in sheep.

Lewisite Oxide: The hydrolysis of Lewisite (2-chlorovinyl dichloroarsine) yields 2-chlorovinyl arsonous acid (CVAA). This loses water to form 2-chlorovinyl arsenous oxide (Lewisite oxide), but this can be quantitatively reversed when the oxide is dissolved in water, or the oxide and the dibasic acid may exist in equilibrium (references 17, 18). Lewisite is considered more toxic than its hydrolysis product and lewisite oxide; however the hydrolysis product retains the trivalent arsenic and much of the toxicity of Lewisite (references 5,19).

For Lewisite oxide, and its hydration product, the RfD developed for Lewisite is suggested as a surrogate. This value is also currently under review by the National Academy of Sciences NRC Committee on Chronic Reference Doses for Selected Chemical Warfare Agents. The proposed RfD is 0.1 ug/kg/day. The RfD for Lewisite was derived from a NOAEL of 0.6 mg/kg/day (time-adjusted to 0.44mg/kg/day) determined in a multi-generational study in rats.

Calculation of Reference Concentration (RfC)

Since there are no inhalation toxicity data on the chemical breakdown products listed in Table 1, The suggested RfC is derived in each case from the RfD calculated above and listed in Table 2. The RfC, calculated as described under Methods, are listed in Table 3, together with the RfD values.

Discussion

In this study, several compounds lacked both laboratory data and QSAR estimates that might serve as starting points for development of provisional RfD values. For each of these compounds, EMPA, EA2192, and lewisite oxide (2-chlorovinyl arsenous oxide), the RfD was estimated using data relating to a closely related, surrogate compound. In each case it is unlikely that the surrogate compound is significantly less toxic than the compound of interest.

In the case of lewisite oxide/ chlorovinylarsonous acid, the use of TOPKAT is not possible because currently available models do not cover metalo-organics. The QSAR estimates for EA2192 and for rat chronic LOAEL in the case of EMPA were not usable because of the 'location' of these molecular structure far outside of the 'optimum prediction space' of the pertinent TOPKAT models.

Usable QSAR estimates were available only for TDG and MPA. In these cases, RfD were estimated on this basis, while for TDG an additional estimate was made from a short term experimental NOAEL value. These two estimates differed by less than a factor of two.

In cases where neither usable laboratory-derived values nor acceptable QSAR estimates are available for chronic or subchronic LOAEL or NOAEL, a short-term or acute toxicity value, such as an LD_{50} may be the only or best endpoint available for the particular compound. The problem of estimating RfD from LD_{50} was studied by Layton et al. ,1987 (18) who analyzed data from a large number of compounds. Their study suggests that, although not a substitute for subchronic or chronic toxicity data, the LD_{50} (mg/kg) can be used to estimate the RfD by multiplying by a factor of 5×10^{-6} to 1×10^{-5}. This approach introduces much uncertainty, because of the wide variability of the ratio LD_{50}/RfD and the possibility that acute and chronic effects may arise through different mechanisms. Derivation from LD_{50} was not used in this study, with the use of a suitable surrogate compound being given preference.

The methods EPA uses in derivation of Reference Concentrations (RfC) are similar in concept to those used for oral RfDs; however, the actual analysis of inhalation exposure is more complex than for oral exposure. This is due to the dynamics of the respiratory system and its diversity across the species and to differences in the physicochemical properties of contaminants. RfCs are derived from NOAELs by applying uncertainty factors similar to those used for oral RfDs as well as appropriate factors for respiratory volume and other factors. The inhalation values derived from oral RfDs are intended to serve as screening levels only. Thus they do not represent EPA guidance (references 2,4).

Summary:

Provisional estimates of Reference Dose (RfD) have been made for five key breakdown products of chemical warfare agents, viz., thiodiglycol (TDG), methyl phosphonic acid, (MPA), ethyl methyl phosphonic acid (EMPA), EA 2192, and lewisite oxide/2-chlorovinyl arsonous acid. The chemicals are identified in Table 1, while the RfD values, with other essential information, are given in Table 2. Laboratory data, apart from acute toxicity information, that was usable for RfD development was available only for TDG. Usable QSAR estimates (of rat chronic LOAEL) were available only for TDG and MPA. For TDG, both the experimental and the QSAR information were used.

For the remaining compounds, EMPA, EA2192, CVAA and Lewisite oxide, information and existing or proposed RfD values from surrogate, closely related compounds were used. For EMPA the existing RfD for isopropyl methyl phosphonic acid (IMPA), currently listed in USEPA's IRIS database, was used as a surrogate. For EA2192, CVAA, and Lewisite oxide, currently proposed RfD's for VX and Lewisite, respectively, are listed. These, when accepted, are probably the best values for these two hydrolysis products.

Suggested inhalation Reference Concentration (RfC) values were calculated from the calculated RfD values. These values are intended for screening purposes only.

References:

1. Enslein, K. 1984. *Estimation of toxicological endpoints by structure-activity relationships.* Pharm. Rev. 36(2): 131S-135S.

2. U.S. Environmental Protection Agency (1989). Risk Assessment Guidance for Superfund. Volume 1, Human Health Evaluation Manual (part A) Interim Final. Office of Emergency and Remedial Response, Washington DC. EPA/540/1-89/002, December 1989.

3. U.S. Environmental Protection Agency (1992). Air/Superfund National Technical Guidance Study Series: Estimation of Air Impacts for the Excavation of Contaminated Soil. USEPA, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-450/1-92-004, March 1992.

4. U.S. Environmental Protection Agency (1994). Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, U.S. EPA, Research Triangle Park, NC. EPA/600/8-90/066F, Oct. 1994.

5. J. Industr. Hyg. & Toxicol. 23: 259, 1941. Registry for Toxic Effects of Chemical Substances (RTECS), 1997, Nat'l Inst. For Occup. Safety & Health.

6. Bausum, HT (in preparation) QSAR Estimates of Toxicity of Chemical Agents and their Breakdown Products. Report Prepared for the USACHPPM Chemical Agent Standards Working Group.

7. Angerhofer, RA. 1997. Subchronic Oral Toxicity of Thiodiglycol in Rats. Phase I. USACHPPM Toxicological Study No. 85-7415-97.

8. Mecler, FJ. 1981. Mammalian Toxicological Evaluation of DIMP and DCPD (Phase 3-IMPA) Litton Bionetics, Inc., contract to US Army Med. R.&D. Command, Ft. Detrick, MD.

9. Proceedings of the International Congress on Toxicology, Toxicology as a Predictive Science, 1st, Toronto, 1977, Plaa, GL & WA Duncan, eds., New York, Academic Press, p. 450.

10. Bucci, TJ et al. 1997. Two-generation reproductive study in mink fed diisopropyl methylphosphonate (DIMP). Study No. TP-001, Final Report. Pathology Associates, Int'l., Jefferson, AR.

11. Williams, RT et al. 1987. Environmental Fate and Effects of Tributyl Phosphate and Methyl Phosphonic Acid, CRDEC-CR-87103: NTIS AD-A184, 959/5; US Army Armament Munitions Chemical Command, Chemical Research, Development & Engineering Center, Aberdeen Proving Ground, MD.

12. US EPA, NCEA, Cincinnati, 1996.) Risk Assessment Issue Paper for: Derivation of an Oral RfD for

Methylphosphonic acid (CASRN 993-13-5). Paper No. 96-024.

13. US EPA. Integrated Risk Information System (IRIS), 1987-1997, Micromedex, Inc.,

14. US Army Ctr. For Health Promotion & Prev. Med., 1996. USACHPPM Technical Guide TG-218, Detailed and General Facts about Chemical Agents.

15. MacNaughton, MG and JH Brewer. 1994. Environmental Chemistry and Fate of Chemical Warfare Agents. Final Report SwRI 01-5864, to US Army Corps of Engineers, Southwest Research Institute, San Antonio, TX.

16. DA, 1996. OTSG Interim Chronic ReferenceToxicological Criteria for Chemical Warfare Compounds. Memorandum, MCHB-DC-C, dated June 4, 1996. Department of the Army, Office of the Surgeon General.

17. Major, MA. 1989. Octanol-Water Partition Coefficients of Surface and Groundwater Contaminants Found at Military Installations, Tech. Rept. TR88-10, US Army Biomed. R.&D. Laboratory, Ft. Detrick, MD.

18. Rosenblatt, DH et al. , 1975. Problem Definition Studies on Potential Environmental Pollutants. Physical, Chemical, Toxicological and Biological Properties of 16 Substances. Technical Report TR-7509, US Army Med. Bioeng. R. & D. Laboratory, Ft. Detrick, MD

19. Layton, DW et al. 1987. Deriving allowable daily intakes for systemic toxicants lacking chronic toxicity data. Regulatory Toxicol. & Pharmacol. 7:96-112.

TABLE 1: Selected Key Breakdown Products of Chemical Agents

Substance	CAS No.	Name	Product of	Structure
TDG	111-48-8	Thiodiglycol	Sulfur mustard	$HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}OH$
MPA	993-13-5	Methyl-phosphonic acid	GB, VX	$CH_3\text{-}P(OH)(OH)=O$
EMPA	1832-53-7	Ethyl methyl-phosphonic acid	VX	$CH_3\text{-}CH_2\text{-}O\text{-}P(OH)(CH_3)=O$
IMPA	1832-54-8	Isopropyl methyl-phosphonic acid	GB	$(CH_3)_2CH\text{-}O\text{-}P(OH)(CH_3)=O$
EA 2192	73207-98-4	S-(2-diisopropylaminoethyl) methylphosphonothioic acid	VX	$((CH_3)_2CH)_2N\text{-}CH_2CH_2S\text{-}P(OH)(CH_3)=O$
Lewisite oxide	3088-37-7	2-chlorovinyl arsenous oxide	Lewisite	$Cl\text{-}CH=CH\text{-}As=O$
CVAA	85090-33-1	2-chlorovinyl arsonous acid	Lewisite	$Cl\text{-}CH=CH\text{-}As(OH)_2$

TABLE 2: Summary of Estimates of Reference Dose for Products of Chemical Agents

Chemical	Basis for Derivation of RfD/ RfC	Safety Factor	mg/kg/da	ug/kg/da
TDG	LOAEL (rat, chronic, QSAR est.) = 1700 mg/kg/da (Ref. 6)	UF = 3000 MF = 3	0.17	170
	14 da NOAEL, rat = 1250 mg/kg/da (Ref. 7)	UF = 3000 MF = 3	0.13	130
	90 da NOAEL, rat = = 500 mg/kg/da (Ref. 7)	**UF = 3000 MF = 1**	**0.17**	**170**
MPA	LOAEL (rat,chronic, QSAR est.) = 566 mg/kg/da (Ref. 6)	UF = 3000 MF = 3	0.057	57
	NOAEL, for IMPA (rat, subchronic) = 279 mg/kg/da (Ref. 12*)	**UF = 10000 MF = 1**	**0.02**	**20**
		*** includes adjustment for MW MPA/IMPA)**		
EMPA	**NOAEL, for IMPA (rat, subchronic) = 279 mg/kg/da (Ref 12)**	**UF = 3000 MF = 3**	**0.028**	**28**
IMPA	**NOAEL = 279 = 279 mg/kg/day (Ref. 12)**	**UF = 3000 MF = 1**	**0.1**	**100**
EA 2192	**LOAEL for VX (sheep, subchronic, Based on ChE inhibition) = 0.06 ug/kg/da**	**UF = 90 MF = 1**	**6 E-7**	**0.0006**
Lewisite oxide/CVAA	**Time-adjusted NOAEL for lewisite (rat, subchronic) = 0.44 mg/kg/da**	**UF = 3,000 MF = 1**	**0.0001**	**0.1**

BOLDED values represent the preferred estimate

TABLE 3. Estimated Reference Concentration (RfC) Values and Corresponding RfD Values.

Compound	RfD ☆ (mg/kg/da)	RfC ★ ($\mu g/m^3$)
TDG	0.17	200
MPA	0.020	24
EMPA	0.028	34
IMPA	0.100	110
EA 2192	0.0000006	0.0007
Lewisite oxide/ CVAA	0.0001	0.11

☆ Values from Table 2, q.v. for derivation.

★ Derived from RfD Values as described under Methods.

APPENDIX F - ANNEX F.2

FROM: MCHB-TS-THE 25Jan, 1999

TO: MCHB-TS-EHRARC, (Attn: Ms. Veronique Hauschild)

SUBJECT: Status of the request to review the oral RfD for the VX hydrolysis product EA2192.

1. General

a) The oral RfD for EA2192 is now set at the same level as that of VX. This is believed to be overprotective because the ionized state of the EA2192 molecule limits its absorption. All dermal absorption and the majority of the compounds sorbed via the oral route are taken up by passive absorption. High polarity diminishes this uptake and ionization such as is seen with EA 2192 strongly inhibits this process. Dermal studies performed with EA2192 have demonstrated that this compound is excluded by the skin to such an extent that no effects were seen at any of the test dosages used. A comparison of the oral LD50 values for VX and EA2192 reveals a similar situation. The oral LD50 for VX is 12 µg/Kg while the oral LD50 for EA2192 is 630 µg/Kg.

b) Despite the above comparisons and the 50 fold higher LD50 of EA2192 we can not recommend a higher RfD at this time. The reason for our decision is that the limited information on the chronic toxicity of this compound. Considerable uncertainty exists as to the mechanism of the chronic toxicity of phosphonate nerve agents at very low doses. Recent evidence suggests that chronic toxicity of organophosphorus compounds may not be totally due to their action on AChE. Moreover, the studies reported by Michel et al. seem to demonstrate the AChE toxicity caused by EA2192 may be more refractory to nerve agent antidote treatment than toxicity induced from other agents. Although the response of a toxicant to an antidote is not considered in establishment of a RfD this evidence provides an indication that the complex formed between EA2192 and AChE may have greater stability than the complex with VX. Because RfD values are designed to provide protection during chronic exposures, it is important to distinguish between chronic and acute effects. Increases in the long term stability of the phosphonate / enzyme complex may have limited effect on acute toxicity but may contribute to higher steady state concentrations of the inactivated enzyme and hence pose a greater potential for chronic toxicity.

2. Time required for this work: 2 hours

3. POC for this review is M. Major, 410-612-7159

GLENN J. LEACH
Program Manager
Health Effects Research

APPENDIX G

TOXICITY OF AGENTS GA AND GD RELATIVE TO THE TOXICITY OF AGENT GB

It was assumed that the relative acute toxicity, expressed as a ratio of the mean LD_{50} values, would also apply to minimum effect levels (MELs). The LD_{50} values for monkeys and rats for all three agents are given in Table G-1. Data for all exposure routes were used except for percutaneous studies. The latter were considered inappropriate because effect levels are likely to be substantially affected by environmental test conditions and the volatility of the individual agent. Even though the absolute toxicity of the agents varies from species to species and also from one exposure route to another, the relative toxicity, as expressed by the ratios of the LD_{50} values, is expected to be similar because the mechanism of action of all three agents is identical. Where more than one LD_{50} value was available for a given species and exposure route, the geometric mean was calculated. The GA/GB and GD/GB ratios for each species were then determined, and the geometric mean for each set of ratios was calculated. The final mean value for GA/GB was 2.65 and the final mean value for GD/GB was 0.63, indicating that in terms of acute toxicity GA is less than half as toxic as GB and GD is about twice as toxic as GB. These ratios are similar to those derived from comparing the potency of the agents to inhibit acetylcholinesterase. The pI_{50} values (negative log of the concentration causing 50% AChE? inhibition), for GA, GB, and GD are 8.6, 8.9, and 9.2 (Dacre, 1984), equivalent to 2.5×10^{-9}, 1.26×10^{-9}, and 6.3×10^{-10} mol/L, respectively. The GA/GB and GD/GB ratios are 1.99 and 0.5, very similar to those derived from the acute lethality data.

Therefore, to estimate the MELs:

MEL of GA = 2.65 x MEL of GB

MEL of GD = 0.63 x MEL of GB

Table G-1. Estimate of the Toxicity of GA and GD Relative to GB

Route	Species	LD_{50} Values (µg/kg)			Ratio of Effect		References		
		GB	GA	GD	GA/GB	GD/GB	GB	GA	GD
Inhal.	monkey	74[a]	187[a]	-	2.53	-	DA, 1974	DA, 1974	-
	rat	220[a]	450[a]	230[a]	2.05	1.05	DA, 1974	DA, 1974	DA, 1974
I.V.	monkey	20	~50	-	~2.5		DA, 1974	DA, 1974	
	rat	39	70	50			RTECS, 1997	DA, 1974	DA, 1974
	rat	45		44.5			DA, 1974		RTECS, 1997
	mean value [b]	42	70	47	1.67	1.12			
Oral	rat	550	3700	400			RTECS, 1995	Grob &	DA, 1974
	rat	600					Grob & Harvey, 1958	Harvey, 1958	
	rat	870-1000					DA, 1974		
	mean value [b]	676	3700	400	5.47	0.59			
Subcut.	rat	103-108	162	71			RTECS, 1997	RTECS, 1997	RTECS, 1997
	rat		~300					DA, 1974	
	mean value [b]	106	220	71	2.07	0.67			
I.M.	monkey	22	34	9.5	1.55	0.43	RTECS, 1997	RTECS, 1995	RTECS, 1997
	rat	108	800	62			RTECS, 1997	Grob &	RTECS, 1997
	rat	112					DA, 1974	Harvey, 1958	
	rat	170					Grob & Harvey, 1958		
	mean value [b]	127	800	62	6 30	0 49			
I.P.	rat	218	~800	98			RTECS, 1997	DA, 1974	RTECS, 1997
	rat	250	490				DA, 1974	RTECS, 1997	
	mean value [b]	233	626	98	2.69	0.42			
OVERALL MEAN VALUE[c]					2.65	0.63			

[a] n LCt_{50} in mg-min/m³ 10-mi

[b] Geometric mean for rat

[c] Overall geometric mean for rats and monkeys combined

APPENDIX H

DERIVATION OF DERMAL ABSORPTION FACTORS FOR CHEMICAL AGENTS IN SOIL

MCHB-DC-THE

January 20, 1998

SUBJECT: Derivation of Dermal Absorption Estimates for Chemical Warfare Agents

FROM: Health Effects Research Program

MEMORANDA FOR Acting Program Manager, EHRARC, (Attn: Ms. Veronique Hauschild)

This document reports an estimation of dermal absorption of the chemical warfare (CW) agents HD, GA, GB, GD, VX and L from soil. It is important to note that dermal absorption of Lewisite from soil would be unlikely because it is not stable in water.

1. General Comments: Improvements in our model for calculation of the dermal adsorption of compounds from soil required recalculation of estimate for hourly absorption of chemical warfare agents from soil. Background information on the model is also included.

2. The publication of the EPA's interim report on "Dermal Exposure Assessment: Principles and Applications" in 1992 was a landmark in the area of risk assessment of soil pollutants. That report compiled the very limited experimental data then available, outlined some guidelines about experimental methods and issued the guidance that accurate predictive models would not be possible until a better understanding of the processes involved and more experimental data were available. The response to this guidance in the EPA regions and at the state level was to begin to handle assessment of this risk by adoption of default values for absorption of compounds from soil. The Army now is often required to use default values for absorption of toxic compounds from soil in the range of 3% to 30%.

Default values of this magnitude grossly overestimate dermal absorption from soil for several reasons. These defaults were established by application of large uncertainty factors to the experimental data that was available in the 1992 EPA report. In addition, the studies referenced in that report commonly used 96 hour exposures in rats and freshly prepared soil/pollutant preparations in their experimental method. Such methods overestimate the results in humans because people have lower dermal absorption rates than rats and people exposed to contaminated soils commonly have dermal exposures of much less than 96 hours. Even more importantly, most soils contaminated by Army operations have been acted on by decades of sun and rain, which have reduced the bioavailability of the pollutants they contain. Recent work in Dr. Martin Alexander's Laboratory at Cornell has demonstrated

that pollutants present in the soil at low concentration are, over time, sequestered in the soil matrix and pore water with concomitant losses in toxicity. These studies show that weathering of soil/pollutant mixtures commonly produces reductions in toxicity from 60 to 100%. This phenomenon is seen even in sterilized soils where metabolism and biological binding processes are absent. It is characteristic of such processes that the sequestered compounds can be recovered quantitatively with modern analytical procedures.

It is also important to note, that the data referenced in the 1992 EPA report were predominately from studies with large, halogenated, hydrophobic compounds having extremely limited aqueous solubility. Chemical warfare agents and most other Army contaminants of concern are smaller, more volatile, and more hydrophilic. It is generally accepted that dermal absorption of an organic compound increases with the octanol/water partition coefficient (Kow), and this value is a function of hydrophobicity. The chemicals used in the USEPA report all had very large Kow values compared to those of the CW agents.

Kow VALUES FOR USEPA COMPOUNDS

1. Hexadecane = > 1.0×10^7	(log Kow > 7)
2. TCDD = 6.31×10^6	(log Kow 6. 8)
3. TCB = 5.0×10^5	(log Kow 5.7)
4. DDT = 9.5×10^5	(log Kow 5.98)

Kow VALUES FOR CW AGENTS

1. GB Kow = 1.99	(log Kow = 0.299)
2. GA Kow = 2.42	(log Kow = 0.38)
3. GD Kow = 66.6	(log Kow = 1.82)
4. VX Kow = 123	(log Kow = 2.09)
5. HD Kow = 23.4	(log Kow = 1.37)
6. 2-chlorovinylarsonous acid = 0.85	(log Kow = -0.07)

Notes: The Kow of Lewisite cannot be determined since this compound is not stable in water. ARMY FM 3-9 reports that "The rate of hydrolysis is rapid for both vapor and dissolved Lewisite and when the humidity is high Lewisite hydrolyzed so rapidly that it is difficult to maintain a concentration sufficient to blister even unprotected skin." Lewisite oxide is the species formed when Lewisite is hydrolyzed and then dried. It is, in turn, converted quantitatively to 2-chlorovinylarsonous acid when dissolved in water. The latter compound represents the Lewisite species actually found in water.

The values given for the log Kow of HD and G-agents (MRICD 1998) are experimentally determined; the value for VX is calculated (Britton and Grant, 1988; Small, 1984). The EPA compounds

listed all have very low vapor pressure and would not tend to evaporate from the skin prior to absorption. The G-agents, however, all have rather high vapor pressures. Indeed, GB evaporates at a rate similar to water.

It becomes clear that accurate prediction of the dermal absorption of CW agents will require a new approach. The magnitude of the exposure must be calculated as a function of the predicted duration of the exposure rather than using data from 96 hour studies and the model must predict sorption from the physical and chemical properties of the individual compounds and from the soils at the site of the contamination.

In developing a new model for prediction of any behavior, selection of a narrow range of conditions so that one process predominates and competing processes can be safely ignored tends to simplify and increase the accuracy of the estimation process. To do this, we have limited our studies to more water soluble compounds and defined our exposure times as 12 hours or less. Imposition of these limits tends to ensure that the principal route of percutaneous transport will be by dissolution of the compounds in water. In such a system, the pollutants leave the soil and are introduced to the skin by the aqueous route. It is well established that the partition of a compound between soil and water (K_{sw}) can usually be described by calculation of the theoretical partition of the compound between organic carbon and water (K_{oc} = mg/g of organic carbon (in soil)/mg per mL in solution) and then correcting this value for the fractional concentration of organic carbon in the soil (f_{oc}).

$$\mathbf{K_{sw} = K_{oc} \times f_{oc}}$$

The most accurate calculation of soil adsorption coefficients for compounds with properties like the CW agents is a simple linear regression using Kow for the independent variable (Lyman et al., 1982).

$$\mathbf{\log Koc = 0.544 \log Kow + 1.377}$$

Thus, Koc values for the CW agents:

GB Koc = 34.6
GA Koc = 38.5
GD Koc = 234
VX Koc = 327
HD Koc = 133

It has also been shown that the rate of penetration (flux) of a compound through the skin relates in a positive fashion to the compound's water solubility (WS) and octanol/water partition coefficient (K_{ow}) and inversely to its molecular weight (MW). Numerous formulas are available to predict this behavior. The formula of Fiserova-Bergerova et al. (1990) shows particular promise in the prediction of the dermal absorption of compounds of moderate solubility in water.

$$\textbf{Hourly flux} = 0.067WS\,(0.038 + 0.153\,K_{ow})\,e^{-0.016MW}$$

FL = Flux (penetration through the skin)
WS = water solubility
Kow = octanol/water partition
MW = molecular weight

The molecular weights (MW) and water solubilities (WS) of the CW agents are:

GB MW = 140.1; WS = miscible (1 g/mL used as default)
GA MW = 162.1; WS = 98 mg/mL
GD MW = 182.2; WS = 21 mg/mL
VX MW = 267.4; WS = 30 mg/mL
HD MW = 159.1; WS = 0.92 mg/mL

Therefore, FL values for the CW agents (given in terms of the amount of agent that will penetrate a square cm of skin in one hour) can be calculated.

GB FL = 2.41 mg/cm^2
GA FL = 0.20 mg/cm^2
GD FL = 0.78 mg/cm^2
VX FL = 0.53 mg/cm^2
HD FL = 1.31 mg/cm^2

In order to link the concepts of soil/water partition and hourly flux together into a model to predict dermal uptake from soil, it is necessary to follow the fate of a quantity of compound through these processes. It is probably not true that one mL of water will obtain equlibrium with one gram of soil; the equlibrium would most certainly be between one mL of water and much less than a gram of soil. However, we will use the one gram number as one means of safe siding this model. It is also inaccurate to assume that soil/water equilibrium will occur more or less instantaneously but we will also make this assumption. Thus, the concentration of pollutant in the soil (mg/g) divided by the K_{sw} yields the concentration of pollutant in water (mg/mL). If we make the additional assumption that the material

moving through 1 cm^2 of skin in one hour is drawn exclusively from this volume (1 mL will form a layer of water over 1 cm^2 of skin that is 1 cm deep), then the flux divided by the amount of compound in the 1 mL of water becomes the fractional absorption in one hour. We can relate these two equations to obtain a formula for calculation of percent absorption from soil per hour.

Percent of soil contaminant absorbed/hour = hourly flux/WS x 100 (1/Ksw)

Using this formula and the chemical-specific FL, WS, and Ksw values given above, the hourly dermal absorption rates for the CW agents were calculated for a soil with 2% organic carbon.

Hourly dermal absorption of CW agents from soil of 2% organic carbon:

GB = 0.35%
GA = 0.26%
GD = 0.78%
VX = 0.27%
HD = 0.70%

Conclusions

1) Sequestration of pollutants in weathered soil makes accurate experimental determination of K_{sw} difficult because the soil/water partition can take months to establish. This process also limits the concentration of toxicants transferred from weathered soils to water during the limited time frames that are characteristic of dermal exposures. Because this model assumes rapid and complete equlibrium between soil and water it will usually overestimate values of hourly flux. Comparison of calculated results with experimental results confirms this contention. Experimental values for dermal absorption of TNT, TNB, RDX, and thiodiglycol, performed with an *in vitro* pig skin system using two different soils, indicate that the model normally overestimates absorption on the order of 2 to 2.5 fold. Similar results were seen *in vivo* in primate studies of absorption of 2,4D from soil. Due to the moderate molecular weight and aqueous solubility of the chemical warfare agents, this model should predict their dermal absorption with good accuracy. However, the blister agent HD will have a much lower dermal transport than predicted because of its reactivity with the skin and its very rapid rate of hydrolysis in aqueous environments (half life is about 4 minutes at body temperature).

2) This is the only model known to this author that has demonstrated accuracy in prediction of the dermal absorption of military significant compounds from soil. USACHPPM is currently seeking acceptance of this model as a predictive tool for risk assessment at military installations. The model has been presented to the EPA's Office of Risk Assessment and will be presented to the risk assessment activity of the Office of The Superfund in Feb. 1998. Use of this model rather than reliance on default values will greatly improve the accuracy of the assessment process and may achieve significant reductions in cleanup costs at military installations.

3) This model uses a minimum default value of 2% organic carbon in the soil. This is because for the purposes of predicting a soil/water partition coefficient, soil has other properties than organic carbon that contribute to the soil/water partition. At high organic carbon concentrations these other properties have a negliable effect on the partition but at low organic carbon concentrations they become more significant.

References

1. Lyman, J.W., W.F. Reehl and D.H. Rosenblatt. 1982. Handbook of Chemical Property Estimation. McGraw-Hill Book Company, New York, NY.

2. Fiserova-Bergerova, V., J.T. Pierce and P.O. Droz. 1990. Dermal Absorption Potential of Industrial Chemicals: Criteria for Skin Notation. American Journal of Industrial Medicine. 17:617-635.

3. Britton, K.B. and C.L. Grant. 1988. Prediction of Octanol-Water Partition Coefficients of Organophosphonates: Evaluation of Structure-Function Relationships. Special Report 88-11, U.S. Army Corps of Engineers Cold Regions Research & Engineering Laboratory, Hanover, NF.

4. Medical Research Institute for Chemical Defense (MRICD). 1998. Personal communication.

4. Small, M.J. 1984. Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate. U.S. Army Medical Bioengineering Research & Development Laboratory, Fort Detrick, Frederick, MD. Technical Report 8304. ADA 149515.

GLENN J. LEACH
Program Manager
Health Effects Research

Military site: http://chemdef.apgea.army.mil /chemcasu/Decontam.htm

DECONTAMINATION

United States Army
Medical Research Institute
of Chemical Defense.
Medical Management of Chemical
Casualties Handbook 2nd ed
September, 1995
Section 8, Decontamination
Chemical Casualty Care Office
APG, MD 21010-5425

OVERVIEW

Decontamination is the reduction or removal of chemical agents. Decontamination may be accomplished by removal of these agents by physical means or by chemical neutralization or detoxification. Decontamination of skin is the primary concern, but decontamination of eyes and wounds must also be done when necessary. Personal decontamination is decontamination of self; casualty decontamination refers to the decontamination of casualties; and personnel decontamination usually refers to decontamination of non-casualties.

The most important and most effective decontamination of any chemical exposure is that decontamination done within the first minute or two after exposure. This is self-decontamination, and this early action by the soldier will make the difference between survival (or minimal injury) and death (or severe injury). Good training can save lives.

Decontamination of casualties is an enormous task. The process requires dedication of both large numbers of personnel and large amounts of time. Even with appropriate planning and training the requirement demands a significant contribution of resources.

Liquids and solids are the only substances that can be effectively removed from the skin. It is generally not possible or necessary to decontaminate vapor. Removal from the atmosphere containing the vapor is all that is required.

Many substances have been evaluated for their usefulness in skin decontamination.

The most common problems with potential decontaminants are irritation of the skin, toxicity, ineffectiveness, or high cost. An ideal decontaminant will rapidly and completely decontaminate all known chemical and biological warfare agents. Furthermore, a suitable skin decontaminant must have certain properties that are not requirements for decontaminants for equipment. Recognized desirable traits of a skin decontaminant include:

•Neutralization of all agents •Safety (compound to be both nontoxic and noncorrosive) •Ease of application by hand •Readily available •Rapid action •Nonproduction of toxic end products •Stability in long-term storage •Short-term stability (after issue to unit/individual) •Affordability •Nonenhancement of percutaneous agent absorption •No irritability •Hypoallergenicity •Ease of disposal

Decontamination issues have been explored since the beginning of modern chemical warfare. After years of research worldwide, simple principles which consistently produce good results still apply.

The first, which is without equal, is timely physical removal of the agent. To remove the substance by the best means available is the primary objective. Chemical destruction (detoxification) of the offending agent is a desirable secondary objective. Physical removal is imperative because none of the chemical means of destroying these agents do so instantaneously. While decontamination preparations such as fresh hypochlorite react rapidly with some agents (e.g., the half-time for destruction of VX by hypochlorite at a pH of 10 is 1.5 minutes), the half-times of destruction of other agents, such as mustard, are much longer. If a large amount of agent is present initially, a longer time is needed to completely neutralize the agent to a harmless substance.

Decontamination studies have been conducted using common household products. The goal of these studies was identification of decontaminants for civilians as well as field expedients for the soldier. Timely use of water, soap and water, or flour followed by wet tissue wipes produced results equal, nearly equal, or in some instances better than those produced by the use of Fuller's Earth, Dutch Powder, and other compounds. (Fuller's Earth and Dutch Powder are decontamination agents currently fielded by some European countries.) This is easily understood because 1) no topical decontaminant has ever shown efficacy with penetrated agent, 2) agents in large enough quantity, especially vesicants, may begin penetrating the skin before complete reactive decontamination (detoxification) takes place, and 3) early physical removal is most important.

Military personnel may be questioned for guidance by local civilian authorities or may deal with supply shortages in the field. Knowledge of the U.S. doctrinal solutions may not suffice in these situations, and awareness of alternative methods of decontamination will prove very beneficial.

However, it is not so much what method is used, rather it is how and when it is used. Chemical agents should be removed as quickly and completely as possible by the best means available.

The M291 resin kit and 0.5% hypochlorite for casualty decontamination are state-of-the-art. The M291 kit is new, whereas hypochlorite has been around since World War I. The M291 kit is the best universal dry decontaminant for skin. Fresh 0.5% hypochlorite solution with an alkaline pH is the best available universal liquid

decontaminating agent. Liquids are best for large or irregular surface areas. Hypochlorite solutions are well suited for medical treatment facilities with adequate water supplies. For hypochlorite to be the best universal liquid skin decontaminant it has to be relatively fresh (made daily or more frequently, particularly in a warm environment where evaporation will occur) and at a concentration of 0.5% at an alkaline pH. Hypochlorite solutions are for use on skin and soft tissue wounds only. Hypochlorite should not be used in abdominal wounds, in open chest wounds, on nervous tissue, or in the eye. Surgical irrigation solutions should be used in liberal amounts in the abdomen and chest. All such solutions should be removed by suction instead of sponging and wiping. Only copious amounts of water, normal saline, or eye solutions are recommended for the eye. Contaminated wounds will be discussed later.

The M291 resin kit is best for spot decontamination of skin only. It rapidly adsorbs the chemical agent with carbonaceous material physically removing the agent from skin contact. Later an ion exchange resin neutralizes the offending agent by chemical detoxification. Since the M291 kit is small and dry and easily carried by the soldier, it is well suited for field use. It will be the early intervention with the use of this kit that will reduce chemical injury and save life in most cases. Decontamination of the casualty using an M291 kit does not obviate the need for decontamination at a field facility. The decontamination station is more conducive to thorough decontamination. Chemical agent transfer is a potential problem that can be resolved by a second deliberate decontamination. Decontamination at the medical treatment facility prevents spread of the agent to areas of the body previously uncontaminated, contamination of personnel assisting the patient, and contamination of the medical facility.

CERTIFICATION OF DECONTAMINATION

Certification of decontamination is accomplished by any of the following: processing through the decontamination facility; M-8 paper; M-9 tape; M256A1 ticket; or by the CAM (Chemical Agent Monitor). If proper procedure is followed the possibility of admitting a contaminated casualty to field medical facility is extremely small. The probability of admitting a dangerously contaminated casualty is miniscule to non-existent. Fear is the worst enemy, not the contaminated soldier.

METHODS OF DECONTAMINATION

Three basic methods of decontamination are physical removal, chemical deactivation, and biological deactivation of the agent. Biological deactivation has not been developed to the point of being practical.

PHYSICAL REMOVAL

Several types of physical and chemical methods are at least potentially suitable for decontaminating equipment and material. Flushing or flooding contaminated skin or material with water or aqueous solutions can remove or dilute significant amounts of agent. Scraping with a wooden stick, i.e., a tongue depressor or popsicle stick, can remove bulk agent by physical means. For the decontamination of clothing only, adsorbents and containment materials (to be used on outer garments before their removal and disposal) have been considered. A significant advantage of most physical methods is their nonspecificity. Since they work nearly equally well on chemical agents regardless of chemical structure, knowledge of the specific contaminating agent or agents is not required.

Flushing with Water or Aqueous Solutions

When animal skin contaminated with GB was flushed with water (a method in which physical removal predominates over hydrolysis of the agent), 10.6 times more GB was required to produce the same mortality rate as

when no decontamination occurred. In another study, the use of water alone produced better results than high concentrations of hypochlorite (i.e., 5.0% or greater, which are not recommended for skin). Timely copious flushing with water physically removes the agent and will produce good results.

Adsorbent Materials

Adsorption refers to the formation and maintenance of a condensed layer of a substance, such as a chemical agent, on the surface of a decontaminant as illustrated by the adsorption of gases by charcoal particles and by the decontaminants described in this section. Some NATO nations use adsorbent decontaminants in an attempt to reduce the quantity of chemical agent available for uptake through the skin. In emergency situations dry powders such as soap detergents, earth, and flour, may be useful. Flour followed by wiping with wet tissue paper is reported to be effective against GD, VX and HD.

M291 Resin

The current method of battlefield decontamination by the individual soldier involves the use of a carbonaceous adsorbent, a polystyrene polymeric, and ion exchange resins (M291). The resultant black resin is both reactive and adsorbent. The M291 Kit has been extensively tested and proven highly effective for skin decontamination. It consists of a wallet-like carrying pouch, containing 6 individual decontamination packets. Each packet contains a non-woven fiber-fill laminated pad impregnated with the decontamination compounds. Each pad provides the individual with a single step, non-toxic/non-irritating decontamination application, which can be used on the skin, including the face and around wounds. Instructions for use are marked on the case and packets. The individual decontamination pads are impregnated with the decontamination compound "Ambergard XE-555 Resin", which is the black, free-flowing, resin based powder. As the pad is scrubbed over the contaminated skin the chemicals are rapidly transferred into and trapped in the interior of the resin particles. The presence of acidic and basic groups in the resin promotes the destruction of trapped chemical agents by acid and base hydrolysis. Because the resin is black it maps out the areas that have been decontaminated.

CHEMICAL METHODS

Three types of chemical mechanisms have been used for decontamination: water/soap wash; oxidation; and acid/base hydrolysis.

HD (mustard) and the persistent nerve agent VX contain sulfur molecules that are readily subject to oxidation reactions. VX and the other nerve agents (GA, GB, GD, and GF) contain phosphorus groups that can be hydrolyzed. Therefore, most chemical decontaminants are designed to oxidize HD and VX and to hydrolyze nerve agents (VX and the G series).

Water/Soap Wash

Both fresh water and sea water have the capacity to remove chemical agents not only through mechanical force but also via slow hydrolysis; however, the generally low solubility and slow rate of diffusion of CW agents in water significantly limit the agent hydrolysis rate.

The predominant effect of water and water/soap solutions is the physical removal or dilution of agents; however, slow hydrolysis does occur particularly with alkaline soaps. In the absence of hypochlorite solutions or other appropriate means of removing chemical agents, these methods are considered reasonable options.

Oxidation/Hydrolysis

The most important category of chemical decontamination reactions is oxidative chlorination. This term covers the "active chlorine" chemicals like hypochlorite. The pH of a solution is important in determining the amount of active chlorine concentration. An alkaline solution is advantageous. Hypochlorite solutions act universally against the organophosphorus and mustard agents.

Both VX and HD contain sulfur atoms that are readily subject to oxidation. Current doctrine specifies the use of a 0.5% sodium or calcium hypochlorite solution for decontamination of skin and a 5% solution for equipment.

Hydrolysis

Chemical hydrolysis reactions are of two types: acid and alkaline. Acid hydrolysis is of negligible importance for agent decontamination because the hydrolysis rate of most chemical agents is slow, and adequate acid catalysis is rarely observed. Alkaline hydrolysis is initiated by the nucleophilic attack of the hydroxide ion on the phosphorus atoms found in VX and the G agents. The hydrolysis rate is dependent on the chemical structure and reaction conditions such as pH, temperature, the kind of solvent used, and the presence of catalytic reagents. The rate increases sharply at pH values higher than 8 and increases by a factor of four for every 10oC rise in temperature. Several of the hydrolytic chemicals are effective in detoxifying chemical warfare agents; unfortunately, many of these (e.g., NaOH) are unacceptably damaging to the skin. Alkaline pH hypochlorite hydrolyzes VX and the G agents quite well.

WOUND DECONTAMINATION

All casualties entering a medical unit after experiencing a chemical attack are to be considered contaminated unless there is certification of non-contamination.

The initial management of a casualty contaminated by chemical agents will require removal of MOPP and decontamination with 0.5% hypochlorite before treatment within the field treatment facility.

Initial Decontamination

During initial decontamination in the decontamination areas bandages are removed and the wounds are flushed; the bandages are replaced only if bleeding recurs. Tourniquets are replaced with clean tourniquets and the sites of the original tourniquets decontaminated. Splints are thoroughly decontaminated, but removed only by a physician.

The new dressings are removed in the operating room and submerged in a 5% solution of hypochlorite or placed in a plastic bag and sealed.

General Considerations

Of the agents discussed, only two types, the vesicants and nerve agents, might present a hazard from wound contamination. Cyanide is quite volatile so it is extremely unlikely that liquid cyanide will remain in a wound, and it requires a very large amount of liquid cyanide to produce vapor adequate to cause effects.

Mustard converts to a cyclic compound within minutes of absorption into a biological milieu, and the cyclic compound rapidly (minutes) reacts with blood and tissue components. These reactions will take place with the components of the wound--the blood, the necrotic tissue, and the remaining viable tissue. If the amount of bleeding and tissue damage is small, mustard will rapidly enter the surrounding viable tissue where it will quickly biotransform and attach to tissue components (and its biological behavior will be much like an intramuscular absorption of the agent).

Although nerve agents cause their toxic effects by their very rapid attachment to the enzyme acetylcholinesterase, they also quickly react with other enzymes and tissue components. As they do with mustard, the blood and necrotic tissue of the wound will "buffer" nerve agents. Nerve agent that reaches viable tissue will be rapidly absorbed, and since the toxicity of nerve agents is quite high (a lethal amount is a small drop) it is unlikely that casualties who have had much nerve agent in a wound will survive to reach medical care.

Potential risk to the surgeon from possibly contaminated wounds arises from agent on foreign bodies in the wound and from thickened agents.

Thickened Agents

Thickened agents are chemical agents that have been mixed with another substance (commonly an acrylate) to increase their persistency. They are not dissolved as quickly in biological fluids, nor are they absorbed by tissue as rapidly as other agents. VX, although not a thickened agent, is absorbed less quickly than other nerve agents and may persist in the wound longer than other nerve agents.

Thickened agents in wounds require more precautions. Casualties with thickened nerve agents in wounds are unlikely to survive to reach surgery. Thickened HD has delayed systemic toxicity and can persist in wounds even when the large fragments of cloth have been removed. Though the vapor hazard to surgical personnel is extremely low, contact hazard from thickened agents does remain and should always be assumed.

No country is currently known to stockpile thickened agents. In a chemical attack, the intelligence and chemical staffs should be able to identify thickened agents and to alert the medical personnel of their use.

Off-Gassing

The risk from vapor off-gassing from chemically contaminated shrapnel and cloth in wounds is very low and not significant. Further, there is no vapor release from contaminated wounds without foreign bodies. Off-gassing from a wound during surgical exploration will be negligible (or zero). No eye injury will result from off-gassing from any of the agents. A chemical-protective mask is not required for surgical personnel.

Foreign Material

The contamination of wounds with mustard or nerve agents is basically confined to the foreign material (e.g., BDU and protective garment in the wound). The removal of this cloth from the wound effectively eliminates the hazard. There is little chemical risk associated with individual fibers left in the wound. No further decontamination of the wound for chemical agent is necessary.

Wound Contamination Assessment

The CAM (Chemical Agent Monitor) can be used to assist in locating contaminated objects within a wound; however, 30 seconds are required to achieve a bar reading. The CAM detects vapor, but may not detect liquid (a thickened agent or liquid on a foreign body) deep within a wound. A single bar reading on CAM with the inlet a few millimeters from the wound surface indicates that a vapor hazard does not exist.

Hypochlorite

Diluted hypochlorite (0.5%) is an effective skin decontaminant for patient use. The solution should be made up fresh daily with a pH in the alkaline range. Plastic bottles containing 6 ounces of calcium hypochlorite are currently fielded for this purpose.

Hypochlorite solution is contraindicated for the eye. This substance may result in corneal opacities. It is also not recommended for brain and spinal cord injuries. Irrigation of the abdomen may lead to adhesions and is therefore also contraindicated. The use of hypochlorite in the thoracic cavity may be less of a problem, but the hazard is still unknown.

Wound Exploration/Debridement

Surgeons and assistants are advised to wear a pair of well fitting (thin) butyl rubber gloves or double latex surgical gloves and to change them often until they are certain there are no foreign bodies or thickened agents in the wound. This is especially important where puncture is likely because of the presence of bone spicules or metal fragments.

The wound should be explored with surgical instruments rather than with fingers. Pieces of cloth and associated debris must not be examined closely, but quickly disposed of in a container of 5% hypochlorite. The wound can then be checked with the CAM which may direct the surgeon to further retained material. It takes about 30 seconds to get a stable reading from the CAM. A rapid pass over the wound will not detect remaining contamination. The wound is debrided and excised as normal, maintaining a no-touch technique. Removed fragments of tissue are dropped into hypochlorite. Bulky tissue such as an amputated limb should be placed in a plastic or rubber bag (chemical proof) which is then sealed.

Hypochlorite solution (0.5%) may be instilled into deep non-cavity wounds following the removal of contaminated cloth. This solution should be removed by suction to an appropriate disposal container. Within a short time, i.e., 5 minutes, this contaminated solution will be neutralized and nonhazardous. Subsequent irrigation with saline or other surgical solutions should be performed.

Penetrating abdominal wounds caused by large fragments or containing large pieces of chemically contaminated cloth will be uncommon. Surgical practices should be effective for the majority of wounds in identifying and removing the focus of remaining agent within the peritoneum. When possible the CAM may be used to assist. Saline, hydrogen peroxide, or other irrigating solutions do not necessarily decontaminate agents, but may dislodge material for recovery by aspiration with a large bore sucker. The irrigation solution should not be swabbed out manually with surgical sponges. The risk to patients and medical attendants is minuscule. However, safe practice suggests that any irrigation solution should be considered potentially contaminated. Following aspiration by suction the suction apparatus and the solution should be disposed of in a solution of 5% hypochlorite.

Superficial wounds should be subjected to thorough wiping with 0.5% hypochlorite and subsequent irrigation with normal saline.

Instruments that have come into contact with possible contamination should be placed in 5% hypochlorite for 10 minutes prior to normal cleansing and sterilization. Reusable linen should be checked with the CAM. M-8 paper, or M-9 tape for contamination. If found to be contaminated it should be disposed of in a 5-10% hypochlorite solution.

CONCLUSIONS

Decontamination at the medical treatment facility is directed toward (1) eliminating any agent transferred to the patient during removal of protective clothing; (2) decontaminating or containing of contaminated clothing and personal equipment; and (3) maintaining an uncontaminated treatment facility.

Current doctrine specifies the use of 0.5% hypochlorite solution or the M291 Kit for contaminated skin. These are both state-of-the-art decontamination preparations, one old and one new.

Fabric and other foreign bodies that have been introduced into a wound have the capacity to sequester and slowly release chemical agent presenting a liquid hazard to both the patient and medical treatment personnel. There is no vapor hazard to surgical personnel. Protective masks are not necessary.

Appendix E
Physical-Chemical Data

The following tables provide physical-chemical data on the agents discussed in this Handbook.

	GA Tabun	GB Sarin	GD Soman	GF	VX
Mole. Wt.	162	140	182	180	267
Vapor Density	5.63	4.86	6.33	6.2	9.2
Liquid Density	1.07 @ 25°C	1.09@ 25°C	1.02@ 25°C	1.17 @ 20°	1.01@ 20°C
Freez/ Melt Point (°C)	-5	-56	-42	-30	<-51
Boil Point (°C)	240	158	198	239	298
Vapor press.	0.037	2.9	0.4	0.04	0.007
Volatility	610	22,000	3,900	438	10.5

	HD Distilled Mustard	L Lewisite	CX Phosgene Oxime
Mole.Wt.	159	207	114
Vapor Density	5.4	7.1	3/9
Liquid density	1.27@ 25°C	1.89@ 20°C	--
Freez/ Melt. Point (°C)	14	-18	35-40
Boiling Point (°C)	217	190	53-54
Vapor Pressure	0.07@ 20°C	0.39@ 20°C	11.2@ 25°C
Volatility	610@ 20°C	4480@ 20°C	1800@ 20°C

	AC Hydrogen Cyanide	CK Cyanogen Chloride	CG Phosgene
Mole. Weight	27	61	99
Vapor Density	0.99	2.1	3.4
Liquid Density	0.69	1.18	1.37
Freez. Melt. Point (°C)	-13.3	-6.9	-128
Boil. Point (°)C	25.7	12.8	7.6
Vapor Pressure Volatility	742@ 25°C 1,080,000 @25°C	1000@ 25°C 2,600,000 @12.8°C	1.17@ 20°C 4,300,000 @7.6°C

	CN Mace	CS
Mole. Weight	155	189
Vapor Density	5.3	--
Liquid Density	1.32 (solid) @20°C	1.04 @20°C
Freez/ Melt. Point (°C)	54	~94
Boiling Point (°C)	249	~310 (with decomposition
Vapor pressure	0.0041 @20°C	0.00034 @20°C
Volatility	34.3 @20°C	0.71 @25°C

INTRODUCTION

PURPOSE

Chemical warfare is not a popular topic, and most military health care providers do not willingly become familiar with it. This was painfully obvious during Operation Desert Shield/Desert Storm when it soon became apparent that many health care providers knew little about the effects of chemical agents or about the medical defense against them. This ignorance was particularly striking in view of the seven-decade-long history of modern chemical warfare and the well-publicized use of mustard and nerve agent during the Iran-Iraq war in the 1980s. The prevailing attitude of military health care providers was that chemical agents would be used only on Hmong, Afghans, Kurds, or similarly unprepared and unprotected groups of people. Further, many health care providers believed if chemical weapons were used the outcome would be disastrous, defense would be impossible, and the casualty rate and loss of life would be high.

Through education, however, medical professionals involved in Operation Desert Shield/Desert Storm learned that medical defenses were possible and effective, that chemical casualties could be saved and returned to duty, and that mortality could be minimized. Further, they realized that they might be the target of chemical agents. More importantly, they rapidly learned that General Pershing's warning (written shortly after World War I) about chemical agents was still true: "...the effect is so deadly to the unprepared that we can never afford to neglect the question."

The purpose of this handbook is to provide a small and concise handbook for attendees at the Medical Management of Chemical Casualties Course. The handbook is small so that it can be easily carried, and the format is such that it can be easily updated. It is not intended to be a definitive text on the management of chemical casualties.

HISTORY OF CHEMICAL WARFARE AND CURRENT THREAT

The use of chemical weapons dates from at least 423 B.C. when allies of Sparta in the Peloponnesian War took an Athenian-held fort by directing smoke from lighted coals, sulfur, and pitch through a hollowed-out beam into the fort. Other conflicts during the succeeding centures saw the use of smoke and flame, and the Greeks during the seventh century A.D. invented Greek fire, a combination

probably of rosin, sulfur, pitch, naphtha, lime and saltpeter. This floated on water and was particularly effective in naval operations. During the fifteenth and sixteenth centuries, Venice employed unspecified poisons in hollow explosive mortar shells and sent poison chests to its enemy to poison wells, crops, and animals.

The birth of modern inorganic chemistry during the late eighteenth and early nineteenth centuries and the flowering of organic chemistry in Germany during the late nineteenth and early twentieth centuries generated both a renewed interest in chemicals as military weapons and also a spirited debate concerning the ethics of chemical warfare. The British admiralty rejected as "against the rules of warfare" a 1812 request to use burning sulfur-laden ships as a prelude to marine landings in France, and 42 years later the British War Office similarly condemned Sir Lyon Playfair's proposal to use cyanide-filled shells to break the siege of Sebastopol during the Crimean War, arguing that to use cyanide was "inhumane and as bad as poisoning the enemy's water supply." (Sir Lyon retorted, "There's no sense to this objection. It is considered a legitimate mode of warfare to fill shells with molten metal which scatters upon the enemy and produces the most frightful modes of death. Why a poisonous vapor which would kill men without suffering is to be considered illegitimate is incomprehensible to me. However, no doubt in time chemistry will be used to lessen the sufferings of combatants.") Other nineteenth-century proposals that were never put into practice included the idea of using chlorine-filled shells against the Confederacy during the American Civil War and the suggestion of Napoleon III during the Franco-Prussian war that French bayonets be dipped into cyanide. The Brussels Convention of 1874 attempted to prohibit the use of poisons in war, and delegates to the Hague Conventions in 1899 and 1907 considered the morality of chemical warfare but were unable to draft more than a weak and vaguely worded resolution against the use of chemicals on the battlefield.

Against the background of this debate, World War I began. Early in the war, German units used the new but as-yet-unreliable invention the portable flamethrower; and France, where gendarmes had successfully employed riot-control agents for civilian crowd control, used small quantities of these agents in minor skirmishes against the Germans. Riot-control agents, although the first chemicals used on a modern battlefield, proved largely ineffective, and the search for more effective riot-control agents continued throughout the war.

It should have been no surprise that the first large-scale use of chemical agents during the war was by heavily industrialized Germany, with its impressive scientific base of theoretical and applied chemistry and its capacity for mass production of chemicals. German units released an estimated 150 tons of chlorine gas from some 6000 cylinders near Ypres, Belgium, during the afternoon of 15 April 1915. Although this attack caused probably no more than 800 deaths, it was psychologically devastating to the 15,000 Allied troops, who promptly retreated. However, the Germans were unprepared to take advantage of this victory, and chlorine and its successors were doomed to play a tactical rather than a strategic role during the war.

Shortly thereafter, the British were ready to respond in kind with chlorine, and the chemical armamentarium of both sides expanded with the addition of phosgene and chloropicrin. These three agents damaged primarily the upper and lower airways, and both sides developed a variety of masks to prevent inhalational injury. Masks also had the potential to protect against cyanide, which the French and the British (but not the Germans) also fielded to a limited extent during the war.

However, on 12 July 1917--again near Ypres, Belgium--German artillery shells delivered a new kind of chemical agent, sulfur mustard, which in that attack alone caused 20,000 casualties and which

generated a series of new problems. Mustard, a relatively nonvolatile liquid, was persistent compared to the previously used agents, and thus not only the air that the soldier breathed but also the objects that he touched became potential weapons. It was effective at low doses. It affected not only the lungs but also the eyes and the skin. Finally, the latent period of up to several hours with mustard meant that there were no immediate clues to exposure as there had been with the earlier agents. Masks had to be augmented by hot, bulky chemical protective clothing for soldiers and protection for their horses. The need for such a protective ensemble made fighting more difficult physically and psychologically. Diagnosis of mustard exposure was difficult, and mustard-exposed soldiers could easily overwhelm the medical system. Because the effects of mustard were delayed and progressive, most mustard casualties eventually presented for medical treatment. Although in most countries fewer than 5% of casualties from mustard who reached medical treatment stations died, mustard injuries were slow to heal and necessitated an average convalescent period of over 6 weeks.

Between World War I and World War II, debate on chemical warfare continued in the United States and in international forums. The wording of the 1925 Geneva Protocol, which all of the major powers except for the United States and Japan ratified, implied the prohibition of the first use (but not the possession) of chemical and biological weapons. The treaty preserved the right to use such weapons in retaliation for a chemical attack. Russia, which had suffered half a million chemical casualties during World War I, worked with Germany in chemical-agent offensive and defensive programs from the late 1920s to the mid-1930s. In contrast, the United States Chemical Corps struggled to stay alive in the face of widespread sentiment against chemical warfare.

Evidence (not all of which is conclusive) suggests that the military use of chemical agents continued after the end of World War I. Following WWI, Great Britain allegedly used chemicals against the Russians and mustard against the Afghans north of the Khyber Pass, and Spain is said to have employed mustard shells and bombs against the Riff tribes of Morocco. During the next decade, the Soviet Union supposedly used lung irritants against tribesmen in Kurdistan; and Mussolini, who utilized tear gas during the war against Abyssinia in 1936 and 1937, also authorized massive aerial delivery of mustard a) against Abyssinian tribesmen and b) as an interdiction movement on Italian flanks. Immediately prior to World War II and during the early part of that war, Japan is supposed to have used chemical weapons against China.

In the late 1930s, a German industrial chemist, Dr. Gerhard Schrader, searching for more potent insecticides synthesized tabun, an extremely toxic organophosphate compound; two years later, he synthesized sarin, a similar but even more toxic compound. During World War II, Nazi Germany weaponized thousands of tons of these potent organophosphates, which came to be called nerve agents. Why they were not used during the war is a matter of continuing discussion. Hitler, himself a mustard casualty during World War I, did not favor their use; neither did his senior staff, who had fought on chemical battlefields during that war. Wrongly concluding from trends in Allied scientific publications on insecticides that the Allies had their own nerve-agent program, German leaders may have been afraid of retaliation in kind to any Axis use of nerve agents (President Roosevelt had in fact announced a no-first-use policy but had promised instant retaliation for any Axis use of chemical agents). Finally, during the later stages of the war, Germany lacked the air superiority needed for effective delivery of chemical weapons. The well-organized German nerve-agent program thus remained a complete secret until its discovery by the Allies during the closing days of the war.

With the possible exception of Japan during attacks on China, no nation during World War II used chemical agents on the battlefield, although Germany employed cyanide and perhaps other chemical agents in its concentration camps. However, over 600 military casualties and an unknown number of

civilian casualties resulted from the 1943 German bombing in Bari Harbor, Italy, of the John Harvey, an American ship loaded with two thousand 100-pound mustard bombs. The 14% fatality rate was due in large part to systemic poisoning following ingestion of and skin exposure to mustard-contaminated water by sailors attempting to keep afloat in the harbor following the attack; civilian casualties, on the other hand, suffered more from the inhalation of mustard-laden smoke.

The end of World War II did not stop the development, stockpiling, or use of chemical weapons. During the Yemen War of 1963 through 1967, Egypt in all probability used mustard bombs in support of South Yemen against royalist troops in North Yemen. The U.S., which used defoliants and riot-control agents in Vietnam and Laos, finally ratified the Geneva Protocol in 1975 but with the stated reservation that the treaty did not apply either to defoliants or to riot-control agents. During the late 1970s and early 1980s, reports of the use of chemical weapons against the Cambodian refugees and against the Hmong tribesmen of central Laos surfaced, and the Soviet Union was accused of using chemical agents in Afghanistan.

Widely publicized reports of Iraqi use of chemical agents against Iran during the 1980s led to a United Nations investigation that confirmed the use of the vesicant mustard and the nerve agent tabun (GA). Later during the war, Iraq apparently also began to use the more volatile nerve agent sarin (GB), and Iran may have used chemical agents to a limited extent in an attempt to retaliate for Iraqi attacks. Press reports also implicated cyanide in the deaths of Kurds in the late 1980s.

Because of the confirmed Iraqi possession and use of chemical agents, preparations for the liberation of Kuwait by the United Nations coalition included extensive planning for defense against possible chemical attacks by Iraq. Even though this threat never materialized, United Nations inspection teams discovered nerve agents and mustard at Al Muthanna (about 80 km northwest of Baghdad) after the February 1991 cease fire. Other chemical stockpiles may yet exist in Iraq, and inspection efforts continue.

Other countries that have stockpiled chemical agents include countries of the former Soviet Union, Libya (the Rapta chemical plant, part of which may still be operational), and France. Over two dozen other nations may also have the capability to manufacture offensive chemical weapons. The development of chemical-warfare programs in these countries is difficult to verify because the substances used in the production of chemical-warfare agents are in many cases the same substances used to produce pesticides and other legitimate civilian products. The U.S. stockpile consists almost entirely of nerve agents (sarin [GB] and VX) and vesicants (primarily mustard [H; HD]). About 60% of this stockpile is in bulk storage containers; 40% is stored in munitions, many of which are now obsolete. Since the Congressional passage of a bill mandating the destruction of all U. S. chemical agents, one incinerator plant has gone into operation at Johnston Atoll, and other facilities are in the planning stages.

The chemical agents most likely to be used on a modern battlefield are the nerve agents and mustard; because of its alleged use by Iraq, cyanide may also pose a danger. Some intelligence analysts also consider the pulmonary intoxicants to be a credible threat.

TERMS

Chemical agents, like all other substance, may exist as solids, liquids, or gases, depending on temperature and pressure. Except for riot-control agents, which are solids at usually encountered temperatures and pressures, chemical agents in munitions are liquids. Following detonation of the

munition container, the agent is primarily dispersed as liquid or as an aerosol, defined as a collection of very small solid particles or liquid droplets suspended in a gas (in this case, the explosive gases and the atmosphere). Thus, "tear gas," a riot-control agent, is not really a gas at all but rather an aerosolized solid. Likewise, mustard "gas" and nerve "gas" do not become true gases even when it is hot enough to boil water (212°F at sea level).

Certain chemical agents such as hydrogen cyanide, chlorine, and phosgene may be gases when encountered during warm months of the year at sea level. The nerve agents and mustard are liquids under these conditions, but they are to a certain extent volatile--that is, they volatilize or evaporate, just as water or gasoline does, to form an often-invisible vapor. A vapor is the gaseous form of a substance at a temperature lower than the boiling point of that substance at a given pressure. Liquid water, for example, becomes a gas when heated to its boiling point at a given pressure, but below that temperature it slowly evaporates to form water vapor, which is invisible. Visible water clouds (steam) are composed not of water vapor but rather of suspensions of minute water droplets--that is, aerosols.

The tendency of a chemical agent to evaporate depends not only on its chemical composition and on the temperature and air pressure but also on such variables as wind velocity and the nature of the underlying surface with which the agent is in contact. Just as water evaporates less quickly than gasoline does but more quickly than motor oil at a given temperature, pure mustard is less volatile than the nerve agent sarin (GB) but more volatile than the nerve agent VX; but all of these agents evaporate more readily when the temperature rises, when a strong wind is blowing, or when they are resting on glass rather than on, for example, porous fabric.

Volatility is thus inversely related to persistence, because the more volatile a substance is, the more quickly it evaporates and the less it tends to stay or persist as a liquid and to contaminate terrain and materiel. The liquid hazard of a persistent agent is generally more significant than the danger created by the small amounts of vapor that it may generate; the converse is true of nonpersistent agents, which may pose a serious vapor hazard but which also evaporate quickly enough not to create a liquid hazard for an extended time. The arbitrary but generally accepted division between persistent and nonpersistent agents is 24 hours, meaning that a persistent agent will by definition constitute a liquid hazard and contaminate surfaces for 24 hours or longer. Such agents, such as mustard and VX, are thus suitable for contaminating and denying terrain and materiel to the enemy. Nonpersistent agents, such as sarin (GB) and cyanide, find tactical employment in the direct line of assault into enemy territory, since they will have evaporated within a day and will no longer contaminate surfaces. These generalizations are obviously subject to the modifying factors of temperature, environmental factors such as wind, and surface characteristics.

Biological effects occur following exposure to chemical agents dispersed as solids, liquids, gases, aerosols, or vapor. Eye or skin injury may follow direct exposure to the suspended solid particles of aerosolized riot-control agents, and inhalation of these agents brings the aerosolized solid in contact with the epithelium of the respiratory tree. Nevertheless, systemic effects from exposure to riot-control agents are rare. Contact of the eyes or, more likely, the skin with liquid nerve or vesicant agents may produce local effects or may lead to absorption and systemic effects. Liquid exposure is the most important hazard associated with persistent agents and necessitates the proper wearing of chemical protective clothing. At low temperatures, hydrogen cyanide (AC), cyanogen chloride (CK), and phosgene (CG) exist as liquids, but because of their high volatility (low persistence) they seldom present a significant liquid hazard unless the area of exposure is large or unless evaporation is impeded by trapping of liquid agent in saturated porous clothing. Penetrating shrapnel or clothing contaminated with liquid chemical agent of any type may also lead to intramuscular or intravenous

exposure and subsequent systemic effects.

Chemical agents in the form of aerosolized liquid droplets, vapor, or gas may directly contact the eyes, the skin, or (through inhalation) the respiratory tree. Local damage is possible at any of these sites, but systemic absorption through dry, intact skin is usually less important than with the other routes. Vapor or gas exposure to the eyes and especially the respiratory tree is the most important hazard associated with nonpersistent agents and necessitates the proper wearing of a mask that provides both ocular and inhalational protection.

Specialized terms refer to the amount of chemical agent encountered during an exposure. The ED_{50} (pronounced "ED50") and the ID_{50} denote the quantities (usually measured as the weight in :g, mg, or g) of liquid agent that will predictably cause effects (E) or incapacitation (I) in 50% of a given group. Similarly, the LD_{50} is the Lethal Dose or quantity (weight) of liquid agent that will kill 50% of a group. Note that the lower the LD_{50}, the less agent is required and thus the more potent is the agent. Because of differences in absorption, the ED_{50} and LD_{50} values for a given agent are site-specific; that is, the LD_{50} for mustard absorbed through dry, unabraded skin is much higher than the LD_{50} for mustard absorbed through the eye.

Comparison of the amounts of chemical agent encountered as aerosol, vapor or gas requires use of the concentration-time product or Ct, which refers to the agent concentration (usually in mg/m^3) multiplied by the time (usually in minutes) of exposure. For example, exposure to a concentration of 4 mg/m^3 of soman (GD) vapor for 10 minutes results in a Ct of 40 mg"min/m^3. Exposure to 8 mg/m^3 for 5 minutes results in the same Ct (40 mg"min/m^3). For almost any given agent (with the notable exception of cyanide, which will be discussed in a separate chapter), the Ct associated with a biological effect is relatively constant even though the concentration and time components may vary within certain limits (Haber's Law); that is, a 10-minute exposure to 4 mg/m^3 of soman causes the same effects as a 5-minute exposure to 8 mg/m^3 of the agent or to a one-minute exposure to 40 mg/m^3. The ECt_{50}, ICt_{50}, and LCt_{50} then correspond for vapor or gas exposures to the ED_{50}, ID_{50}, and LD_{50}, respectively, for liquid exposure and are likewise site-specific. However, the concentration-time product does not take into account variables such as respiratory rate and depth and is therefore not an exact measure of inhalational exposure.

CHEMICAL AGENTS

Five type of agents will be discussed in this handbook.

Nerve agents inhibit the enzyme acetylcholinesterase and effects are the result of excess acetylcholine. Nerve agents to be discussed are GA (tabun), GB (sarin), GD (soman), GF, and VX.

Vesicants include mustard (sulfur mustard; H; HD), Lewisite (L), and phosgene oxime (CX). Vesicants are so named because of the vesicles (blisters) they cause on the skin; however, these agents also damage the eyes and airways by direct contact and have other effects.

Cyanide has an undeserved reputation as a good warfare agent. Its LCt_{50} is large, and exposures slightly below the lethal Ct cause few effects. Its high volatility means that effective concentrations

are difficult to achieve on the battleground, and that even high concentrations cannot be maintained for more that a few minutes in the open air. However, at high concentrations cyanide kills quickly. Potential agents are hydrocyanic acid (AC) and cyanogen chloride (CK).

Lung-damaging agents include the WWI agent phosgene. The remainder of these agents are hazards of conventional warfare rather than chemical weapons. They include perflurorisobutylene (PFIB), a product of Teflon7 combustion (Teflon7 lines many military vehicles); HC smoke (a smoke containing zinc); and oxides of nitrogen (from burning munitions).

Riot control agents have been used on the battlefield, although they are not considered major agents of threat today. However, the National Guard may encounter or employ them during civil disturbances. The major ones are CS, which is used by law enforcement officials and the military, and CN (Mace7), which is sold in devices for self-protection.

HANDBOOK ORGANIZATION

The next five chapters deal with medical management of casualties from each of the five major groups of chemical agents. Following those chapters is a brief description of procedures for casualty management in a contaminated area. This is followed by a discussion of the principles of decontamination and a chapter describing equipment needed for chemical agent detection, protection, and self-decontamination. The appendix contains procedures for decontamination of litter and ambulatory casualties. The appendix also contains tables listing relevant physicochemical properties and estimated toxicity data for these chemical agents, a diagram of the contaminated receiving area at a field medical facility, a diagram of the Personnel Decontamination Station, and a table briefly describing the agents.

J. Chem Soc. 18-22 (1950)

small amount of insoluble oil. On cooling, there separated from the light petroleum 0·5 g. of a white crystalline adduct, which was twice recrystallised from 140 ml. of light petroleum, yielding 0·38 g. of adduct, m. p. 62—63° (undepressed by the maleic anhydride adduct of α-elaeostearic acid, m. p. 62—63°).

(iv) *Preparation of maleic anhydride addition compound of α-elaeostearic acid.* α-Elaeostearic acid (2·78 g., 0·01 mol.), $E^{1\%}_{1cm.}$ 1795 at 270·6 mμ, was heated with maleic anhydride (1·0 g., 0·0102 mol.) at 108° for 15 minutes. The adduct was separated and recrystallised as above, yielding 0·91 g. of colourless adduct, m. p. 62—63° (Morrell and Samuels, *J.*, 1932, 2251, record m. p. 62·5°). The ultra-violet absorption spectra of this compound and the adduct *from* the concentrates of the triene acid were *identical*.

Linolenic and oleic acid. Preparation of a concentrate of linoleic and oleic acid. The mixed acids (210 g.) from the oil were crystallised *from* 2·5 l. of light petroleum at −70°, and the resultant liquid acids (80·5 g.) were recrystallised from 400 ml. of light petroleum at −60°. The filtrate from *this* crystallisation [11·9 g.; I val. (Toms), 135·6], *which* contained linoleic 17·3, parinaric 3·2, α-elaeostearic 15·2, and conjugated *dienoic* acids 8·5%, was employed for the characterisation of oleic and linoleic acid.

(i) *Bromination (detection of linoleic acid).* The concentrate (3·05 g.) was brominated in 60 ml. of light petroleum at −10° with 0·82 ml. of bromine. The clear liquid was decanted from the deposited oil and set aside overnight at 0°. 0·29 G. of crystalline bromides separated. *The latter were* recrystallised from 10 ml. of ether at −40°, yielding 0·102 g. *of* 9 : 10 : 12 : 13-tetrabromostearic acid, m. p. 113·5—114° alone or mixed *with authentic* tetrabromostearic acid, m. p. 114°. Complete solubility of the bromides in ether indicated the absence of hexabromostearic acid, and hence of *linolenic acid from* the oil.

(ii) *Oxidation with dilute alkaline permanganate.* The concentrate (7·37 g.) was oxidised by *the* method of Lapworth and Mottram (*J.*, 1925, 127, 1628). There were *recovered* 1·83 g. of hydroxy-acids and 2·23 g. *of saturated* and unoxidised acids. On recrystallisation of the former from water and ethyl acetate, 0·80 g. of dihydroxystearic acid, m. p. 132°, was obtained (*mixed* m. p. with 9 : 10-dihydroxystearic acid, m. p. 132°, undepressed). *In addition* the two 9 : 10 : 12 : 13-tetrahydroxystearic acids, *m. p.* 163° (0·32 g.) and 173° (0·13 g.), formed by the oxidation of linoleic acid, were also recovered.

The author thanks *Professor* T. P. Hilditch, F.R.S., for his valuable suggestions and criticism, and Mr G. Winter of the Munition Supply Laboratories, Victoria, Australia, for *gifts of oil and* seeds and for information communicated *privately*.

Department of Industrial Chemistry,
The University, Liverpool.

[*Received, June 28th*, 1949.]

---

5. *Hydrolyses and Derivatives of Some Vesicant Arsenicals.*

By William A. Waters and J. Howarth Williams.

The hydrolyses of pure 2-chlorovinyldichloroarsine (Lewisite-I) and of phenyldichloroarsine have been studied by using the partitions of their solutions between benzene and water. Several dialkyloxy derivatives of Lewisite I, and some analogous dithiols, have been made, and it has been found that dithiocarbamates are particularly useful for characterising the arsenical vesicants.

Lewisite-1 gives a characteristic solid with dioxan, and arsenic trichloride with thioxan.

Hydrolysis of β-Chlorovinyldichloroarsine.—The hydrolysis of Lewisite-I by water involves the following equilibria:

$$\text{ClCH:CH·AsCl}_2 + 2\text{H}_2\text{O} \overset{\text{(fast)}}{\rightleftharpoons} \text{Cl·CH:CH·As(OH)}_2 + 2\text{HCl}$$

$$\underset{\text{(I.)}}{\text{Cl·CH:CH·As(OH)}_2} \overset{\text{(slow)}}{\rightleftharpoons} \text{H}_2\text{O} + \underset{\text{(II.)}}{\text{Cl·CH:CH·AsO}} \overset{\text{(slow)}}{\rightleftharpoons} \underset{\text{(III.)}}{(\text{Cl·CH:CH·AsO})_n}$$

The only substance which can be isolated is polymerised 2-chlorovinylarsinoxide (*III*), a white *insoluble* powder of indefinite m. p. Measurements of the equilibria, however, indicate that both the hydroxide (I) and the unpolymerised oxide (*II*) must be capable of existence in solution in water and benzene respectively.

On treatment with water, Lewisite-I immediately gives a strongly acid solution and a sticky gum, consisting of unchanged Lewisite and (III). If however Lewisite-I is mixed with benzene and then treated with water two clear liquid layers are obtained which, when shaken, rapidly attain an equilibrium which is independent of the initial concentration of the Lewisite-I in the benzene layer. Both the layers can be analysed for (i) chlorine content, (ii) acidity, and (iii) tervalent arsenic by titration with silver nitrate, alkali, and iodine, respectively, and in this way the equilibria attained in the hydrolysis can be found. Figs. 1 and 2 show the results obtained.

The equilibrium attained on shaking a benzene solution of Lewisite-I with aqueous hydrochloric acid corresponds exactly to that reached on shaking a corresponding amount of Lewisite-I with a proportionately smaller volume of water; that is, the percentage of Lewisite-I which

remains as such in the benzene layer depends only on the acidity, the bulk of the aqueous layer being immaterial.

Fig. 1. Fig. 2.

Hydrolysis of Lewisite-I in benzene at 17° in ½ hour.

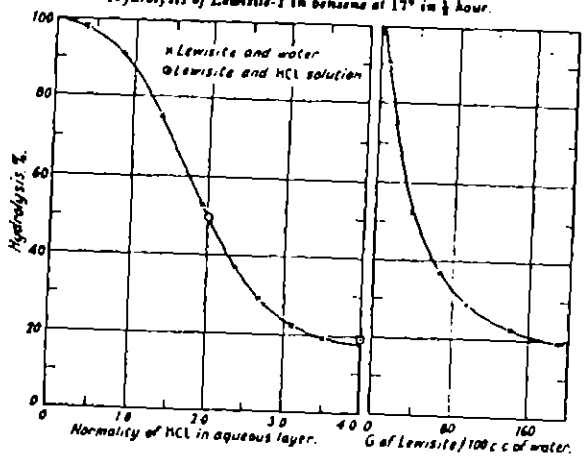
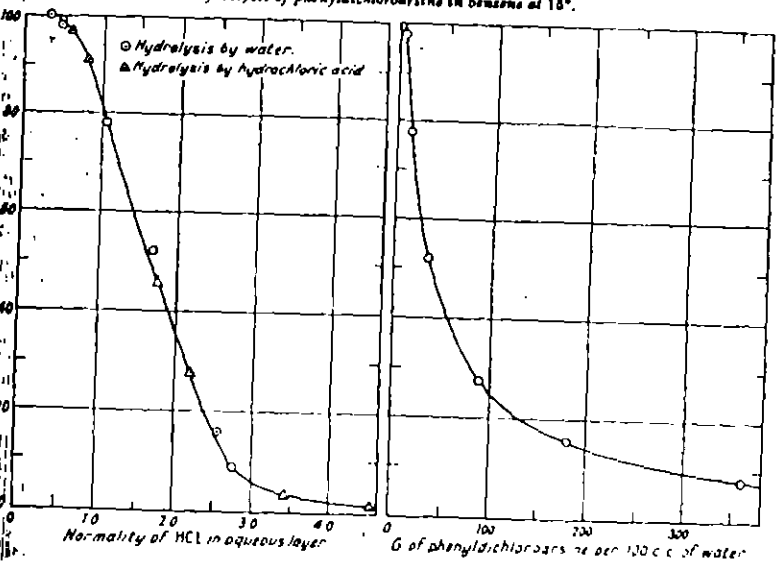


Fig. 3. Fig. 4.

Hydrolysis of phenyldichloroarsine in benzene at 18°.



The hydrolysis of phenyldichloroarsine has been studied in a similar way, giving results which are shown in Figs. 3 and 4.

The evidence for the separate existence of the dihydroxide (*I*) is as follows. A 4% solution

of Lewisite-I oxide (possibly II) in benzene can be obtained by boiling the dry polymerised oxide (III) for a long time with this solvent. The solution is vesicant, and on storage deposits colourless crystals which soon change to the amorphous white polymer. When this benzene solution is shaken with water the arsenic content of the benzene drops *slowly* during some hours. Only a 1% solution of lewisite oxide in water can be obtained by leaving the constituents in contact. When this solution is shaken with benzene the arsenic content of the benzene slowly rises during some hours. The aqueous solution has a pH of 6·8, but by allowing Lewisite-I to remain in contact with water containing chalk a 2·8% solution can be obtained; and a solution of still higher normality can be obtained in aqueous sodium hydrogen carbonate of pH about 8. Thus the dihydroxide of Lewisite-I is, like that of phenyldichloroarsine, a very weak acid giving soluble salts.

Lewisite-I however is decomposed by *cold* caustic alkali as follows:

$$Cl\cdot CH{:}CH\cdot As(OH)_2 + (OH)^- \longrightarrow Cl^- + C_2H_2 + As(OH)_3$$

In the cold (16°), only alkaline solutions of pH 10·5 or more will bring about this decomposition, but at 50° solutions of pH 9 or more are effective. Prolonged boiling with water alone brings about some decomposition of Lewisite-I oxide.

It is significant that the curves shown in Figs. 1—4 show no irregularities indicative of the existence of hydroxy-chlorides R·AsCl·OH.

Alkyl-oxy- and -thio-derivatives of Lewisite-I and its Analogues.—The vesicant character of arsenicals such as Lewisite-I and phenyldichloroarsine is not a property of the $AsCl_2$ group, since carefully prepared solutions of the corresponding oxides or dihydroxides are equally vesicant. In order to enhance the lipoid solubility of 2-chlorovinyldihydroxyarsine and its analogues, a number of derivatives of the general type $R\cdot As(OR')_2$ has been made by the action of sodium alkoxides on the arsenical vesicants. The products are all volatile, vesicant, liquids which are hydrolysed *irreversibly* on contact with water.

A number of analogous thioethers $R\cdot As(SR')_2$ has also been made. These are very slightly soluble in water and in general are hydrolysed *reversibly*, giving toxic, and sometimes vesicant, solutions, though the equilibrium $R\cdot As(SR')_2 + 2H_2O \rightleftharpoons R\cdot As(OH)_2 + 2R'SH$ generally favours thioether formation (cf. Cohen, King, and Strangeways, *J.*, 1931, 3043; Barber, *J.*, 1932, 1365).

Aqueous and alcoholic solutions of sodium diethyldithiocarbamate, and its analogues, react readily with Lewisite-I to give crystalline solids of sharp melting-point which are very useful for the characterisation of the arsenical war gases. These dithiocarbamates are much more stable than are the simple thioethers of the alkyldichloroarsines, but only in cyclic structures, such as that given by "B.A.L." (Peters, Stocken, and Thompson, *Nature*, 1945, 156, 616) does the degree of hydrolysis become negligible. Alkali hydrolyses all these compounds rapidly, acetylene being evolved from the Lewisite-I derivatives. Hydrogen peroxide also breaks up the ethers and thioethers in neutral or acid solution, giving free arsonic acids which are much less toxic than the corresponding tervalent substituted arsines.

Compound Formation with Dioxan.—When pure Lewisite-I is mixed with an equimolecular proportion of dioxan, heat is evolved and the whole mass solidifies on cooling to an addition product, m. p. 58—59°. This however dissociates into its constituents both when vaporised and when dissolved in anhydrous solvents such as benzene or chloroform. Di-2-chlorovinylchloroarsine (Lewisite-II) and tri-2-chlorovinylarsine (Lewisite-III) do not give similar products, and hence Lewisite-I may be separated in this way from these associated compounds. Arsenic trichloride also forms crystalline addition compounds with both dioxan and thioxan, but few of the other arsenical war gases, such as ethyldichloroarsine and phenyldichloroarsine, seem to react. The arsenic trichloride–dioxan adduct has been previously described by Doak (*J. Amer. Pharm. Soc.*, 1934, 23, 641).

Experimental.

Quantitative Hydrolysis of Lewisite-I and Phenyldichloroarsine.—The results shown in Figs. 1—4 were obtained by dissolving a weighed amount of carefully fractionated Lewisite-I or phenyldichloroarsine in 50 ml. of benzene and shaking the solution with a known volume of water for ½ hour at 17°. Figs. 1 and 3 show the relation between the amount of the vesicant, $R\cdot AsCl_2$, which remains as such in the benzene layer and the acidity attained by the aqueous layer.

The points indicated as "hydrolysis by hydrochloric acid" show that the degree of hydrolysis depends on the acidity of the aqueous phase and not on its total volume. Figs. 2 and 4, which refer to hydrolysis by water alone, show the extent to which the vesicants are hydrolysed on admixture with limited quantities of water. Again the degree of hydrolysis is independent of the initial concentration in the benzene layer.

Arsine, AsR_3	B. p.	Formula	Found: C %	H %	As %	Cl %	Equiv.	Required: C %	H %	As %	Cl %	Equiv.
Dimethoxy-2-chlorovinyl-	58°/6 mm.	$C_4H_8O_2ClAs$				17·8	98·6				17·9	99·2
Diethoxy-2-chlorovinyl-	71°/3 mm.	$C_6H_{12}O_2ClAs$				15·5	113				16·7	113
Diisopropoxy-2-chlorovinyl-	80°/3 mm., 88°/6 mm.	$C_8H_{16}O_2ClAs$				13·6	127				13·9	127
Diamyl-2-chlorovinyl-	130—138°/3 mm.	$C_{12}H_{24}O_2ClAs$					165					155
Diisoacyl-2-chlorovinyl-	184—186°/2 mm.	$C_{12}H_{24}O_2ClAs$				13·9	198				14·2	197
Diallyl-2-chlorovinyl-	99°/4 mm.	$C_8H_{12}O_2ClAs$				11·4	125				11·3	156
Di-(2-alkoxyethoxy)-2-chlorovinyl-	150°/3 mm.	$C_{10}H_{20}O_4ClAs$					153					157
Dimethoxyvinyl-	129°/760 mm.	—				44·1					44·4	
Methoxydiphenyl-	138°/2 mm., 160°/7 mm.	$C_{13}H_{13}OAs$					130					130
Methyldimethoxy-	111°/760 mm.	$C_3H_9O_2As$					76					76
Methyldiethoxy-	137°/760 mm.	$C_5H_{13}O_2As$				40·4	89				40·7	90
Methyldimethylthio-	75—77°/2 mm.	$C_3H_9S_2As$				24·6					24·6	
Methyldi-β-hydroxyethylthio-	196—198°/1 mm.	$C_5H_{13}S_2As$										
Diphenylthio-2-chlorovinyl-	230°/0·6 mm.	$C_{14}H_{12}ClS_2As$										
	180—190°/2 mm. (decomp.)										(S, 19·0)	
Di-(NN-diethyldithiocarbamylthio)-2-chlorovinyl- [1]	m. p. 87°	$C_{15}H_{28}ClS_4N_2As$	32·6	5·1	17·4			33·3	5·1	17·3		
Di-(morpholino-4-thiocarboxythio)methyl- [2]	m. p. 178°	$C_{11}H_{19}O_2S_4N_2As$	32·0	4·65	18·0			31·9	4·6	18·1		
Di-(morpholino-4-thiocarboxythio)ethyl- [2]	m. p. 184°	$C_{12}H_{21}O_2S_4N_2As$	33·6	5·0	17·3			33·6	4·9	17·6		
Di-(morpholino-4-thiocarboxythio)-2-chlorovinyl- [2]	m. p. 181°	$C_{12}H_{18}O_2ClS_4N_2As$	31·3	4·0	16·2			31·3	3·9	16·3		
Di-(morpholino-4-thiocarboxythio)phenyl- [2]	m. p. 218—219°	$C_{16}H_{21}O_2S_4N_2As$	40·6	4·45	15·9			40·3	4·4	15·8		

[1] $[O<([CH_2]_2>N\cdot CS\cdot S)_2AsR$. [2] $(NEt_4\cdot CS\cdot S)_2As\cdot CH{:}CHCl$. crystd. from EtOH (Found: S, 29·6%). [3] Needles from aqueous acetone. [4] Prisms from aqueous acetone. [5] Highly refracting rectangular plates. [6] Small needles or spherical aggregates.

Partition Coefficient of Lewisite-I Oxide.—The solution of the oxide in water was shaken with benzene, and samples of each layer, removed at intervals, were analysed for arsenic by addition of excess of iodine and back-titration with standard arsenite solution in the presence of sodium hydrogen carbonate. The following figures show that the equilibrium between the benzene-soluble oxide and the water-soluble dihydroxide is attained only slowly.

	Partition coefficient, $C_{H_2O}/C_{C_6H_6}$.			
Time of shaking (mins.)	10	60	120	1020
Initial aqueous solution + Benzene	8·13	4·74	2·63	1·67
Initial benzene solution + Water	0·07	0·23	0·26	0·69

The influence of the hydrogen carbonate buffer on the partition coefficient is shown by the following figures:

Lewisite + benzene + excess of aqueous $NaHCO_3$: $C_{H_2O}/C_{C_6H_6}$ 13·5
Lewisite oxide (II or III) in benzene + aqueous $NaHCO_3$: $C_{H_2O}/C_{C_6H_6}$ 13·4

Fission of Lewisite-I by the Hydroxyl Ion.—Lewisite-I hydroxide solution was prepared by adding 1 g. of Lewisite-I to 400 ml. of very dilute sodium hydrogen carbonate solution, shaking the mixture until reaction was complete, and acidifying cautiously with dilute hydrochloric acid until pH 7 was reached (B.D.H. Universal Indicator). 10-Ml. samples of this solution were added to 20 ml. of a buffer and maintained at 17°. Fission was detected by adding to each solution 1 ml. of ammoniacal cuprous chloride solution. A reddish-brown precipitate of cuprous acetylide indicated that fission had occurred. Results were:

Buffer used.	Reaction time (hours) before test.			
	2	6	17	24
4% Na_2HPO_4, pH 8·5	—	—	—	—
4% Borax, pH 9·5	—	—	Trace	Slight
4% K_2CO_3, pH 10·5	+	+	+	+

From similar experiments at 50° it was found that at this temperature fission was appreciable at pH 9·5 after 1 hour; 1% (or stronger) solutions of sodium carbonate gave evidence of fission at 50° after only 15 minutes.

A 4% solution can be obtained by boiling Lewisite-I oxide (III) with water for some time; if, however, the evolved vapours are led into ammoniacal cuprous chloride solution a positive acetylene reaction is obtained though a solution of Lewisite-I oxide prepared in the cold gives no positive reaction with this reagent.

Lewisite-I itself, when similarly boiled with water, gives no positive reaction for acetylene.

When administered (*a*) as droplets of Lewisite to the skin, (*b*) by injection, or (*c*) as dihydroxide by mouth, to experimental animals, Lewisite-I is slowly excreted in the form of its water-soluble dihydroxide and can be detected throughout the digestive system and particularly in the urine, by the cuprous chloride reaction which is sensitive to 0·001 mg. and can be used for approximate quantitative assay.

Derivatives of Lewisite-I and its Analogues.—The new compounds shown in the table were prepared in the course of this investigation. Values recorded as As,% were determined iodometrically after destruction of organic matter. The values recorded as equiv. were obtained by titrating the compound directly with iodine, to covert ter- into quinque-valent arsenic.

Adducts with Dioxan and Thioxan.—When equimolar amounts of Lewisite-I and dry dioxan were mixed, considerable heat was generated and, on cooling, the mixture solidified to a mass of white crystals. Recrystallised from light petroleum (b. p. 40—60°) the *compound* formed long colourless needles, m. p. 58—59° [Found: C, 24·3; H, 3·5%; equiv. (As), 146, 148; equiv. (Cl), 148·5. $C_6H_{10}O_2Cl_2As$ requires C, 24·37; H, 3·86%; equiv. (Cl or As), 147·5]. The "equiv. (As)" was determined as recorded above. The "equiv. (Cl)" was determined by titration in acid solution with silver nitrate, which reacts only with the chlorine bound to arsenic. The complex is almost completely dissociated in solution, as shown by molecular-weight determinations: Found: (cryoscopic in benzene) 145; (ebullioscopic in benzene) 195, 198; (ebullioscopic in chloroform) 124. Required: 124.

The arsenic trichloride dioxan complex, prepared in the same way, formed colourless crystals, m. p. 68—70°, from light petroleum, and had the composition assigned to it by Doak (*loc. cit.*) [Found: C, 23·0; H, 3·8%; equiv. (As), 158; equiv. (Cl), 105·0. Calc. for $3(C_4H_8O_2),2AsCl_3$: C, 22·9; H, 3·8%; equiv. (As), 156·6; equiv. (Cl), 104·4]. The molecular weight (cryoscopic in benzene) was 119; the required value is 627, so that the substance is strongly dissociated in solution, as stated by Doak.

The *arsenic trichloride–thioxan* complex, similarly prepared, formed colourless needles, m. p. 70—72° [Found: C, 16·8; H, 2·78%; equiv. (As), 143·5; equiv. (Cl), 96·0. $C_4H_8OSCl_3As$ requires C, 16·8; H, 2·8%; equiv. (As), 142·6; equiv. (Cl), 95·1]. Molecular-weight determination (cryoscopic in benzene) gave a value of 147 (Required: 285), again indicating almost complete dissociation.

The authors express their thanks to Mr. W. E. Hanby for assistance in the study of the hydrolysis of phenyldichloroarsine and to Mr. T. V. Healy for help in the preparation of a few of the dithiols. They thank the Chief Scientific Officer of the Ministry of Supply for permission to publish this paper, which describes work which was completed in 1939—40.

CHEMICAL DEFENCE EXPERIMENTAL STATION
(MINISTRY OF SUPPLY).

[*Received, August 3rd*, 1949.]

CHEMICAL REVIEWS

Volume 92

1992

CHREAY 92[redacted]

ISSN 0009-2665

Decontamination of Chemical Warfare Agents

Yu-Chu Yang,* James A. Baker, and J. Richard Ward

Decontamination Systems Division, Physical Protection Directorate, U.S. Army Chemical Research, Development and Engineering Center (CRDEC), Aberdeen Proving Ground, Maryland 21010-5423

Received January 20, 1992 (Revised Manuscript Received September 17, 1992)

Contents

I. Introduction

Decontamination, aimed at eliminating the hazard of chemical warfare agents, is required on the battlefield as well as in laboratories, pilot plants, and chemical agent production, storage, and destruction sites. The majority of research is focused on battlefield conditions where speed and ease of application of the decontaminant are essential. Battlefield decontamination is the rapid removal of chemical agents from military vehicles, equipment, personnel, and facilities by both chemical and physical methods. Consequently, a solid surface on which chemical agents are deposited is the primary target for decontamination. The nature of the surface and the surface–agent interactions are major concerns in the design of a decontamination system.[1] Some surfaces can be easily penetrated by agents and the embedded agents are more difficult to remove than those residing on the surface.[2] Variables affecting agent diffusion such as contamination time (residence time of the agent on the surface), temperature, and contamination density (the surface density of the agent in mass per unit surface area) are also important parameters for the design of the decontamination process. Furthermore, the decontaminants must not be corrosive so that the surfaces are not damaged after decontamination. It is clear that both chemistry and engineering are required in the design of a decontamination system.

In this review, the chemical reactions of four major chemical warfare agents (1–4, Scheme I) with both the existing field decontaminants and the decontamination systems currently under investigation are described. These chemical agents are the focus of this review because of the toxicities and persistencies of these agents[3] and because of the large stockpile quantities of 1–3. HD (1) is a blistering agent that attacks the mucous membranes and is lethal at high doses.[4] The "nerve" agents VX (2), GB (3), and GD (4) can stop respiratory and nervous functions and can kill in minutes. VX as well as GB consists of two stereoisomers, whereas GD has four stereoisomers, although not all the stereoisomers are responsible for the observed toxicities.[5] The reaction chemistry of these agents is shared by a range of organic compounds such as bivalent sulfides, alkyl chlorides, organophosphorus esters, and pesticides. Since most of these compounds also react with the decontaminants, there is a broad interest in decontamination chemistry from the chemical community. For example, oxidation of sulfur has been used to detoxify HD; nucleophilic substitution at the pentavalent phosphorus has been used to detoxify the nerve agents 2–4; and enzymes have been used to catalyze the hydrolysis of the G agents (2 and 3).

Since the kinetics and mechanisms of the above organic and enzymatic reactions are strongly affected by the solvent property, the solvent system of a decontaminant (i.e. decontamination medium) is an important controlling variable for the decontamination reaction. An optimum medium is one that can both dissolve the agents and promote the desired reaction. Furthermore, the medium is sometimes required to dissolve the "thickened" agent. Chemical agents such as HD and GD are often "thickened" by mixing with 5–10% of a polymer (thickener).[6] The thickened agents are more viscous and adhere better to surfaces than the "neat" agents, making themselves more difficult to remove. It was observed that upon contact with water, a polymer film can form at the interface of the thickened agent and water. This interfacial phenomenon prevents the thickened agent from dissolving into most aqueous solutions. The possible presence of a thickener in the agent adds a significant constraint to the design of the decontamination medium.

Reactive decontaminants are usually more effective than the nonreactive ones because agent removal is more complete at increased speed. However, depending on the resources available on the battlefield, decontamination can also be accomplished by physical methods such as mechanical forces, dissolution, evaporation, or absorption in the absence of any chemical conversions. For example, a surface can be decontaminated by

Yu-Chu Yang was born in China and grew up in Taiwan. She holds a B.S. in Chemical Engineering from the National Taiwan University (1969) and a Ph.D. in Physical Chemistry from Tulane University (1974). After graduation, she worked for Exxon Corp. as a staff chemist and process engineer for nearly six years. She then taught and pursued research as an associate professor at the Department of Chemical Engineering and Technology, National Taiwan Institute of Technology for two years. In 1983, she was granted a Senior Associateship Award by the National Research Council and began research work in decontamination at the U. S. Army CRDEC. She is now a Research Chemist at the Center and has studied both the fundamental and the applied aspects of decontamination for the past nine years. She is best known for her detailed kinetic and mechanistic studies of the reactions of the chemical agents HD and VX.

James A. Baker was born in rural Illinois and obtained his B.S. degree in Chemistry from the University of Missouri at Rolla in 1964. He then went to the University of Wisconsin (Madison) to work with Prof. H. Muxfeldt on natural product synthesis. Muxfeldt moved his group to Cornell University in 1967 and Jim finished his Ph.D. thesis on the total synthesis of 1-deoxylycorine in 1969. After a brief tour in the Army he joined the staff of Edgewood Arsenal. For the last four years he has been the Chief of the Decontamination Systems Division at the U.S. Army CRDEC. On October 1, 1992, he became the Chief Scientist of Research and Technology and is responsible for the basic research programs in chemical and biological defense at the Center

scrubbing, spraying with a soap solution, spraying with a steam jet, or covering with carbonaceous materials. Although only the reactions of agents with decontaminants are emphasized in this paper, one should be aware that battlefield decontamination can also be achieved by nonreactive systems.

II. Development of Decontamination Systems

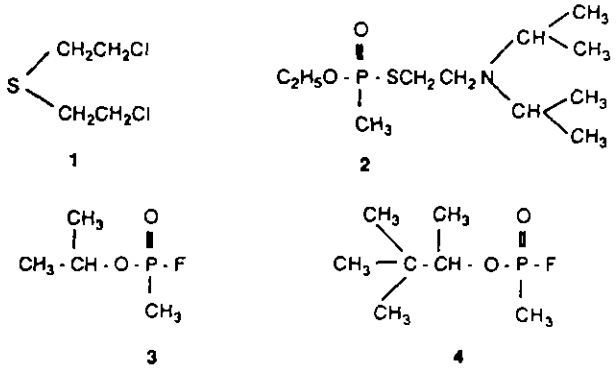
A. Early Decontaminants

The requirement for chemical agent decontamination dates back to World War I when Germany unleashed HD on Allied troops at Ypres, France in 1915.[7] Prior to that time, the poisonous chemicals used on the battlefield, such as chlorine, were nonpersistent gases and required no decontamination. The first decontaminants used were bleaching powders (see Table I) and, to a lesser extent, potassium permanganate. The reactions of chemical agents with excess bleach are so vigorous[8] that both neat and thickened agents can be converted to less or nontoxic products at the liquid–liquid (bleach solution) or liquid–solid (bleach powder) interface in a few minutes. Solubilization of the agents in the same medium as the bleach is not required. As shown in Scheme II, HD is converted into a series of oxidation and elimination products. It is believed that the sulfoxide (**1a**) is formed first, followed by sulfone (**1b**) formation. Subsequently, both oxidation products undergo elimination reactions in the strongly basic solution to produce the corresponding monovinyl and divinyl sulfoxides and sulfones, although small amounts of additional unidentified products are also present in the final solution.[9]

By World War II, superchlorinated bleaches, as shown in Table I, were the most common general purpose decontaminants. However, there are some disadvantages to using bleach as a decontaminant: (a) the active chlorine content of the bleach gradually decreases with

J. Richard Ward received his undergraduate training in Chemistry at the University of Delaware graduating with a B.S. in 1964. He did his graduate studies under Professor Albert Helm at Penn State University and at the State University of New York at Stony Brook obtaining his Ph.D. in 1969. He fulfilled an ROTC commitment through service in the Army Chemical Corps in 1969–1970. He accepted a position as a research chemist with the U.S. Army Ballistic Research Laboratory (BRL) at Aberdeen Proving Ground, MD, in 1971. After ten years at BRL, he moved to the Chemical Research, Development and Engineering Center (CRDEC) where he performed research on the decontamination of chemical agents. He is presently Chief of the Chemical Division in the Research Directorate of CRDEC.

Scheme I. Structures of HD, VX, GB, and GD[a]

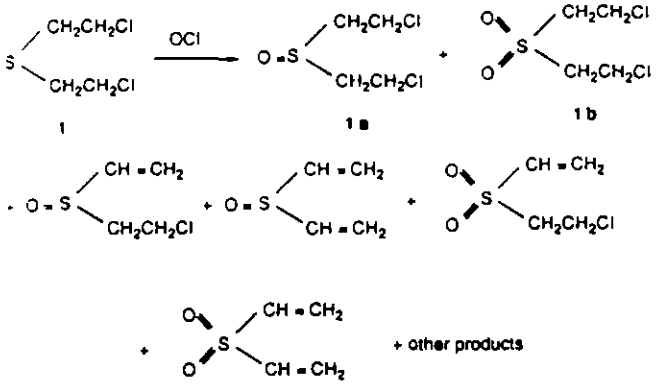


[a] (1) 2,2′-Dichlorodiethyl sulfide (H, HD, mustard, mustard gas, S mustard, or sulfur mustard). (2) *O*-Ethyl *S*-2-(diisopropylamino)ethyl methylphosphonothiolate (VX). (3) 2-Propyl methylphosphonofluoridate (GB or Sarin). (4) 3,3-Dimethyl-2-butyl methylphosphonofluoridate (GD or Soman).

Table I. Decontaminants Composed of Hypochlorites

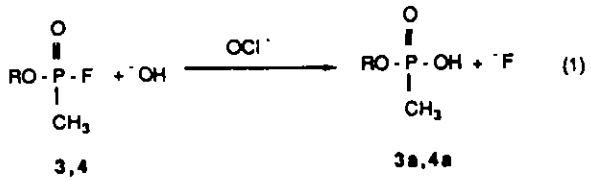
decontaminant	composition	applications
bleach	2–6 wt % NaOCl in water	skin and equipment
HTH (high test hypochlorite)	$Ca(OCl)Cl + Ca(OCl)_2$ as a solid powder or a 7% queous slurry	equipment and terrain
STB (super tropical bleach)	$Ca(OCl)_2 + CaO$ as a solid powder or as 7, 13, 40, and 70 wt % aqueous slurries	equipment and terrain
Dutch powder	$Ca(OCl)_2 + MgO$	skin and equipment
ASH (activated solution of hypochlorite)	0.5% $Ca(OCl)_2$ + 0.5% sodium dihydrogen phosphate buffer + 0.05% detergent in water	skin and equipment
SLASH (self-limiting activated solution of hypochlorite)	0.5% $Ca(OCl)_2$ + 1.0% sodium citrate + 0.2% citrate acid + 0.05% detergent in water	skin and equipment

Scheme II. Reaction Products from HD and Hypochlorite Anion



storage time so that a fresh solution must be prepared prior to each use; (b) a large amount of bleach is required for the oxidation of the agents; and, most importantly, (c) bleach is corrosive to many surfaces. As a result, buffered bleach solutions, as shown in Table I, and the more stable, less alkaline N-chloro compounds (i.e., chloramines or Fichlor, to be discussed later) have been used to overcome some of these difficulties.

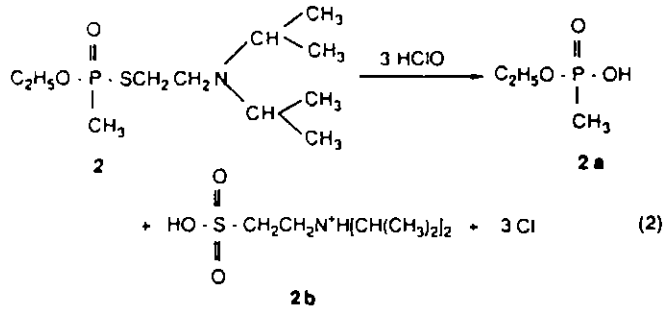
Following World War II, the Allied countries discovered German research efforts on G agents which inhibit acetylcholinesterase (AchE)[3] and are more lethal than HD. These G agents were found to be rapidly detoxified in solutions of alkali salts (e.g., Na_2CO_3, NaOH, or KOH) by conversion to the corresponding phosphonic acids as shown in eq 1.[10] Since acid is



(1)

produced, excess hydroxide ion is required for the reaction to go to completion rapidly. Furthermore, these G agents could also be rapidly detoxified in bleach solutions. As reported by Epstein et al.,[11] the hypochlorite anion behaved as a catalyst for the reaction shown in eq 1.

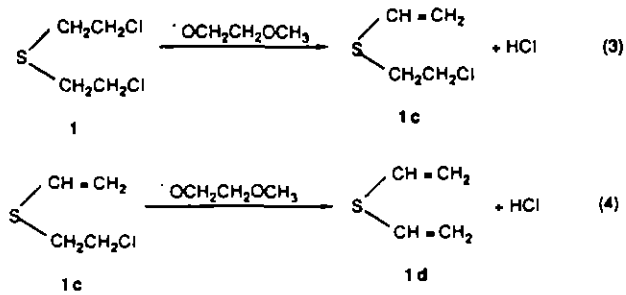
Bleach can also be used for the decontamination of VX particularly under low pH. VX readily dissolves in acidic solutions via protonation of the nitrogen while the sulfur is oxidized by HClO rapidly. As shown in eq 2, only 3 mol of active chlorine are consumed for each mole of VX. At high pH, on the other hand, the solubility of VX is significantly reduced. The deprotonated nitrogen is oxidized accompanied by the evolution of chlorine or oxygen gas and the formation of sulfate and carbonate salts. More than 10 mol of active chlorine are required to oxidize 1 mol of VX under these basic conditions. Despite the long history of alkaline bleach solutions as general purpose decontaminants for the chemical warfare agents, the precise *stoichiometry at high pH has not been determined for* VX.[12]



(2)

B. Decontamination Solution 2 (DS2)

After World War II, the search for a new decontaminant began as a result of the concern over the ineffectiveness of bleach solutions in cold weather operations. Development of the new decontaminant was initiated in 1951, and the result, DS2, was adopted in 1960.[13] DS2 is a general purpose, ready to use, reactive decontaminant with long-term storage stability and a large operating temperature range (−15 to 125 °F or −26 to 52 °C). This polar, nonaqueous liquid is composed, by weight, of 70% diethylenetriamine (**5**, $H_2NCH_2CH_2NHCH_2CH_2NH_2$), 28% ethylene glycol monomethyl ether (**6**, $CH_3OCH_2CH_2OH$), and 2% sodium hydroxide. The reactive component in DS2 was found to be the conjugate base of **6**, $CH_3OCH_2CH_2O^-$ (**6a**). At ambient temperatures, **6a** reacts instantaneously with all four agents. The reactions with HD are shown in eqs 3 and 4. Since both reactions are

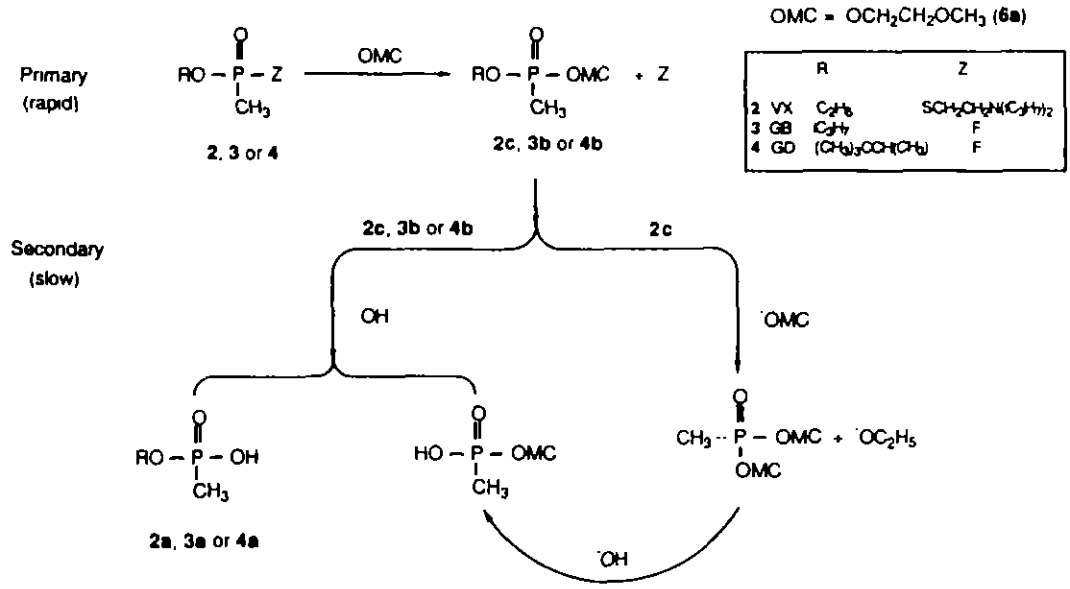


(3)

(4)

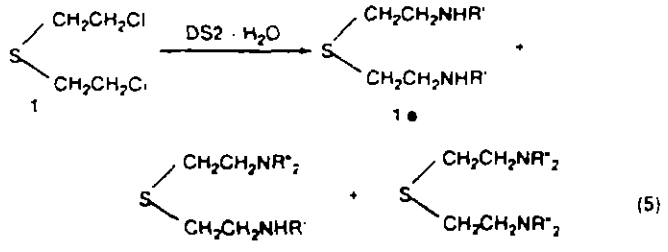
complete within 1 min at room temperature, **1d** from double elimination was observed as the only product,

Scheme III. Reactions of VX, GB, and GD with DS2



while 1c was predicted as an intermediate.[14] The nerve agents 2–4 also react with 6a rapidly to form the diesters 2c, 3b, and 4b as the primary products in Scheme III. With time, these diesters further decompose in DS2 via slower secondary reactions to form 2a, 3a, 4a, and other final products.[14] These reactions are less important since the agents have already been detoxified by the primary reaction.

While DS2 is a highly effective decontaminant and is noncorrosive to most metal surfaces, it can damage paints as well as plastics, rubber, and leather materials. To minimize these problems, the decontamination contact time of DS2 with most painted surfaces is limited to 30 min, followed by a water rinse. DS2 is also corrosive to skin, and 6 has demonstrated teratogenicity in rats. Personnel handling DS2 are required to wear respirators with eye shields and chemically protective gloves in order to avoid skin contact. After exposure to air or to relatively large amounts of water, DS2 rapidly degrades. The carbon dioxide in air is quickly absorbed by 5 to form colloidal ammonium carbonates which cause the solution to become viscous. When sufficient amounts of water are added to DS2, the reactant 6a is deactivated to 6. HD is most sensitive to the depletion of 6a in DS2. Instead of reacting with 6a via elimination, HD reacts slowly with 5 by an S_n1 mechanism to form predominantly 1e and small amounts of related substitution products shown in eq 5.[14]



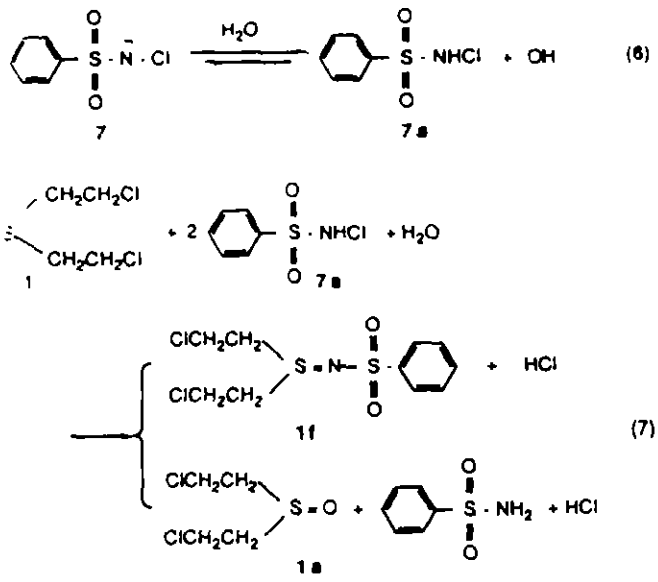
(5)

R' = $CH_2CH_2NCH_2CH_2NH_2$ and R" = $CH_2CH_2NH_2$

C. Decontaminants for Skin and Personal Equipment

The earliest decontaminants used on skin utilized bleaches, usually in dry form, in which the hydrochlorite salt was diluted with an inert solid such as silica. In 1973, a personal decontamination kit was recovered from Soviet vehicles used by Egypt in the Yom Kippur War.[15] This kit was reputed to be very effective against thickened GD. The Army mimicked the decontamination reaction in the Soviet kit and produced the M258 system in 1974 as well as the M258A1 and M280 systems in the 1980s (Table II). These kits consist of two sealed packets. Packet I contains a towelette prewetted with a decontamination solution of 72% ethanol, 10% phenol, 5% NaOH, 0.2% ammonia, and about 12% water by weight. Packet II contains a towelette impregnated with chloramine-B ($PhS(O)_2NClNa$, 7, see eq 6) and a sealed glass ampule filled with a solution of 5% $ZnCl_2$, 45% ethanol, and 50% water by weight. The ampule in packet II is broken and the towelette wetted with the solution immediately prior to use. The two wetted towelettes are used consecutively to wipe skin and personal items such as contaminated masks, hoods, gloves, overboots, and weapons.

Towellete I is effective against the G agents via rapid nucleophilic substitutions at the phosphorus. The fluoride ion in 3 or 4 is displaced by the phenoxide, ethoxide, and hydroxide anions to form, respectively, the corresponding diesters and the methylphosphonic acid 3a or 4a as shown in eq 1.[16a] The same reactions with VX are very slow. Towellete II is designed to decontaminate both HD and VX by rapid oxidation with 7. The oxidation proceeds by a different mechanism than that observed with bleach. As shown in eq 6, 7 dissolves in water to produce 7a and ^-OH; the pK_a of 7 is 9.5.[17] However, the presence of the $ZnCl_2$ maintains the pH of solution II between 5 and 6. The sulfur in HD attacks the chlorine in 7a to form a transient chlorosulfonium ion which rapidly reacts with the anion $PhS(O)_2N^-H$ to form the sulfimide (1f, eq 7), and with H_2O to form mustard sulfoxide (1a). The observed overall reaction is shown in eq 7.



(6)

(7)

VX, which contains a tertiary amino group (pK_a = 9), reacts with the chloramine-B only when the solution is sufficiently acidic so that both reactants are protonated. It was found that VX did not react with the chloramine-B in towellete II because the pH of the solution appeared to be increased by the presence of VX.[16a] In practice, VX is believed to be physically removed from the skin or equipment by the wiping action and by solubilization in the solution. A recent study[16b] showed that in an unbuffered aqueous solution of 0.2 M 7, about 50% of the 0.01 M VX hydrolyzed within a few days. At this point, sufficient acidic products are accumulated to protonate 7 which then reacted rapidly with the remaining VX. The study further showed that 0.01 M VX reacted with 0.1 M 7 in the presence of 0.25 M H_2SO_4 to give a pseudo-first-order rate behavior (Figure 1). In addition to the phosphonic and sulfonic acids (**2a** and **2b**, respectively), a sulfimide **2d** (see Scheme IV) is also produced in the final reaction mixture.[16b] This indicates that, similar to the reaction with HD, the first step in the VX oxidation is also the formation of a chlorosulfonium ion intermediate. This intermediate rapidly reacts with both the anionic sulfonamide and H_2O to form the observed products.

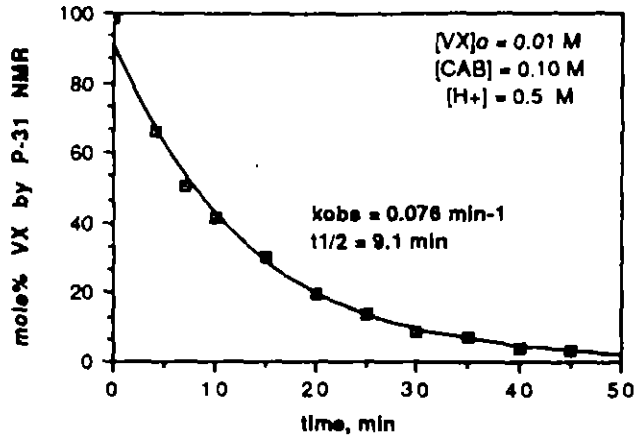
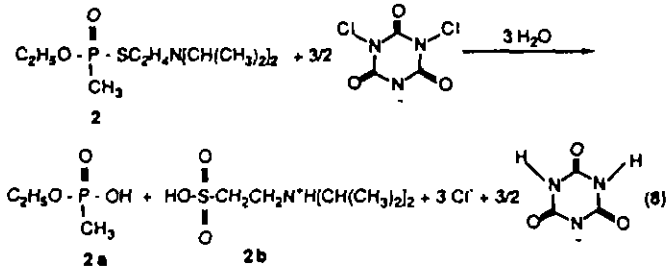


Figure 1. Reaction profile of VX and chloramine-B in acidic solution at 18 °C.

On the other hand, an aqueous solution of a commercial *N*-chloro oxidant, Fichlor (sodium *N,N*-dichloroisocyanurate) detoxifies VX effectively by simple oxidation according to eq 8. Similar to bleach at low pH, HClO is believed to be the reactive species. Since the pH of the Fichlor solution is about 6, detoxification of G agents by this method is too slow to be effective.



(8)

Table II contains a summary list of the decontamination systems and equipment currently available in

Scheme IV. The Reaction of VX and Chloramine-B in Acidic Solution

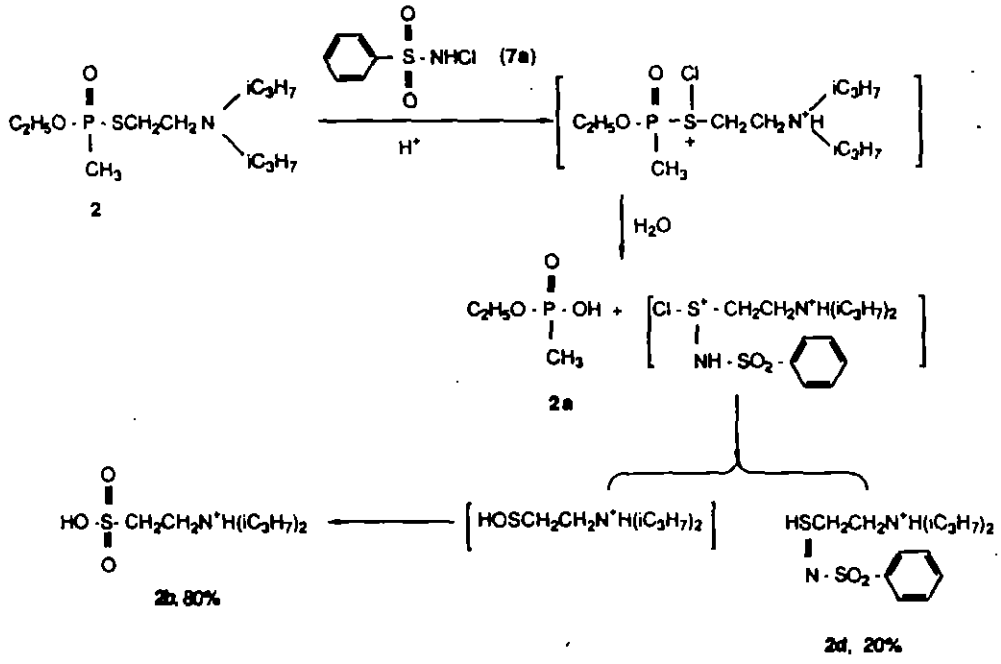


Table II. Field Decontamination Equipment and Systems

item name	description	decontaminants	applications
ABC-M11, decontaminating apparatus, portable	a fire extinguisher-like device to spray DS2; Comes with mounting bracket for attaching to vehicles	1.5 qt (1.3 L) DS2	vehicle and equipment
ABC-M12A1, decontamination apparatus, power-driven, skid-mounted	includes pump, tank, personnel shower units, and M2 water heater	water, foam, deicing liquid, DS2, or STB	washing, deicing, and showering
M258A1, decon kit, personal	consists of foil-packaged pairs of towelettes in a plastic carrying case	I. water, phenol, NaOH, ethanol, and ammonia II. water, ethanol, chloramine-B, and $ZnCl_2$	skin and individual equipment
M280, decon kit, individual equipment	consists of 20 foil-packaged pairs of towelettes in a plastic carrying case	I. water, phenol, NaOH, ethanol, and amminia II. water, ethanol, chloramine-B, and $ZnCl_2$	individual equipment
M291, skin decon kit	consists of 6 foil-packaged nonwoven fiber pads filled with XE-555 resins	2.8 g of XE-555 resins of a total water content of 25 wt %	skin
M13, decon apparatus, portable	self-contained device with a disposable 14-liter DS2 container; can be mounted to the standard fuel can which mounts on vehicles and equipment	DS2	vehicle and equipment
M17, transportable, lightweight, decon system	draws water from any natural source within 30-ft distance and less than 9-ft below pump level; delivers water at pressures up to 689 kPa and temperatures up to 120 °C; includes hoses, cleaning jets, personnel showers, and collapsible rubberized fabric tank	water	equipment, vehicle, and personnel

the U.S. Army inventory. The health hazard posed by the standard decontaminant, DS2, along with the extensive use of nonmetal materials (e.g. laminates and composites) for military equipment has intensified the need for a new liquid decontaminant. The discussion that follows highlights some of the recent research efforts aimed at identifying better decontamination systems.

III. Fundamental Reactions of Agents

In research laboratories, agent–decontaminant reactions are frequently investigated by monitoring the disappearance of agent in the decontaminant. The laboratory techniques are usually titrametric methods, GC, or GLC analyses of the agent in quenched, diluted, and solvent-extracted samples. Novel reaction paths and unstable reaction intermediates are difficult to detect by such methods. The recent application of high-field, multinuclear FTNMR, GC/MS, and direct exposure probe mass spectrometry (DEP/MS) techniques has shed new light on the reaction chemistry of agents. As will be presented in the following sections, parallel and competing reaction pathways as well as the formation of complicated reaction intermediates have been found in many of the fundamental reactions of the agents. This improved understanding of agent chemistry has made the evaluation and prediction of new decontamination systems much more accurate.

A. Chemical Agent Simulants

In order to gain a more complete understanding of agent chemistry, it is often necessary to study the reactions of a series of agent analogs under the same conditions. For example, the monofunctional derivatives of mustard, $RSCH_2CH_2Cl$ (8, R = methyl, ethyl, or phenyl) and $RSCH_2CH_2X$ (X = tosylate, brosylate, Br^-, I^-, or other leaving group), react via the same mechanisms as those of HD, but their reaction products and kinetic rate expressions are much simpler. The use of simulants makes it easier to isolate the variables that affect the agent chemistry. As discussed in the following sections, a VX analog, $(C_2H_5O)(CH_3)P(O)(SC_2H_5)$ (9, see eq 11), has also been studied to isolate the effect of the diisopropylamino group on the reaction chemistry of VX. Similarly, the reactions of a series of organophosphorus esters similar to the G agents [e.g., DMMP (dimethyl methylphosphonate), DIMP (diisopropyl methylphosphonate), DFP (diisopropyl phosphorofluoridate), and NPDP or PNPDPP (*p*-nitrophenyl diphenylphosphate)] have also been extensively investigated as model substrates. Over the past years, reaction studies of these model compounds at university and industrial laboratories have contributed significantly to the development of new decontamination systems.

Each of these simulants, however, can only mimic certain aspects of the reactivity of the specific agent. One must always be aware of the differences, both qualitatively and quantitatively, between the agents and their simulants. One must also be careful not to assume the results from the simulants automatically apply to the agents. In fact, the subtle differences between the simulants and the agent often lead to new discoveries of the chemical nature of the agent. Therefore, in selecting an agent simulant, it is important to determine which property of the agent is to be addressed. For each property, there are many simulant choices, but it is virtually impossible to simulate all the properties of an agent with a single compound.

B. Hydrolysis

1. GB and GD

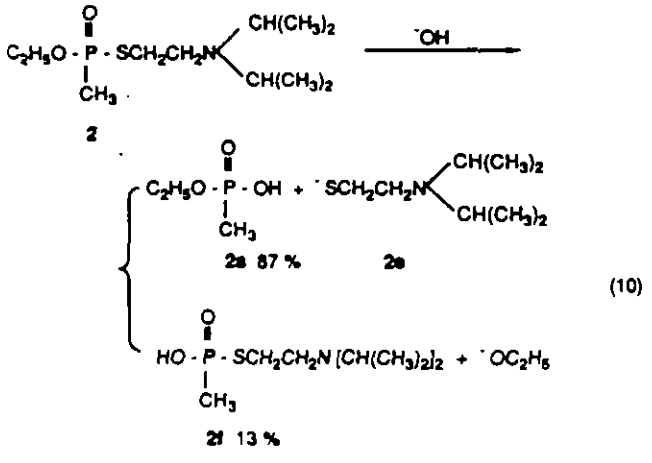
Since all four of the agents under consideration react with water, it would be ideal if hydrolysis could be used as the principal decontamination reaction. However, in order for this to be possible, significant amounts of the agent have to be soluble in water. Both GB and GD dissolve in water, and their hydrolyses under acidic, neutral, and basic conditions have been reported.[10] In dilute solutions, a general equation for the observed hydrolysis rate constant, k_{obs}, can be expressed as

$$k_{obs} = k_w + k_a[H^+] + k_b[^-OH] \quad (9)$$

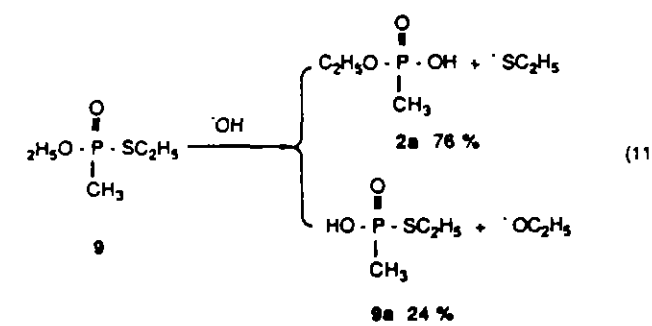
where k_a and k_b are the acid and base hydrolysis rate constants, respectively, and k_a is much smaller than k_b.[10] The rate constant of neutral hydrolysis, k_w, is small compared with the rates under either acidic or basic conditions. At pH values greater than 10, as previously discussed, both GB and GD are hydrolyzed within a few minutes to their corresponding phosphonic acids (see eq 1). Since acids are produced, excess base must be present to maintain the same hydrolysis rate. It is important to note that field decontamination always involves reactions in concentrated solutions. Greater amounts of agent (10^{-2}–10^{-1} M) than those typically used in the laboratory (10^{-5}–10^{-3} M) for kinetic studies are present in the mixture.[19] The kinetics of decontamination reactions usually deviate from first-order behavior since only a small excess of the reactive component is used in the decontaminant.

2. VX

VX ($pK_a = 9$) dissolves in pure water to form a basic solution, and the solubility of VX decreases significantly as the solution becomes more basic. The hydrolysis of 0.01 M VX takes place slowly in parallel paths even at pH 13.[20] As shown in eq 10, one of the reaction paths



(10)



(11)

leads to the formation of the stable but extremely toxic compound, **2f**. Therefore, unlike the G agents, VX cannot be detoxified by base-catalyzed hydrolysis. Similarly, eq 11 shows that a 0.01 M **9** hydrolyzes in the same manner in 0.1 M NaOH. The product ratio from 0.01 M **9** remains constant at 74:26 (P–S P–O bond cleavages) over the range 0.1–1.0 M NaOH, and when the polarity of the solvent changes from pure water to up to 50 vol % *tert*-butyl alcohol or acetonitrile in water. Contrary to Epstein's prediction,[20a] the product ratio is not determined by the pK_a ratio of the two leaving groups, $^-SC_2H_5$ ($pK_a \sim 12$) and $^-OC_2H_5$ ($pK_a \sim 16$).

3. HD

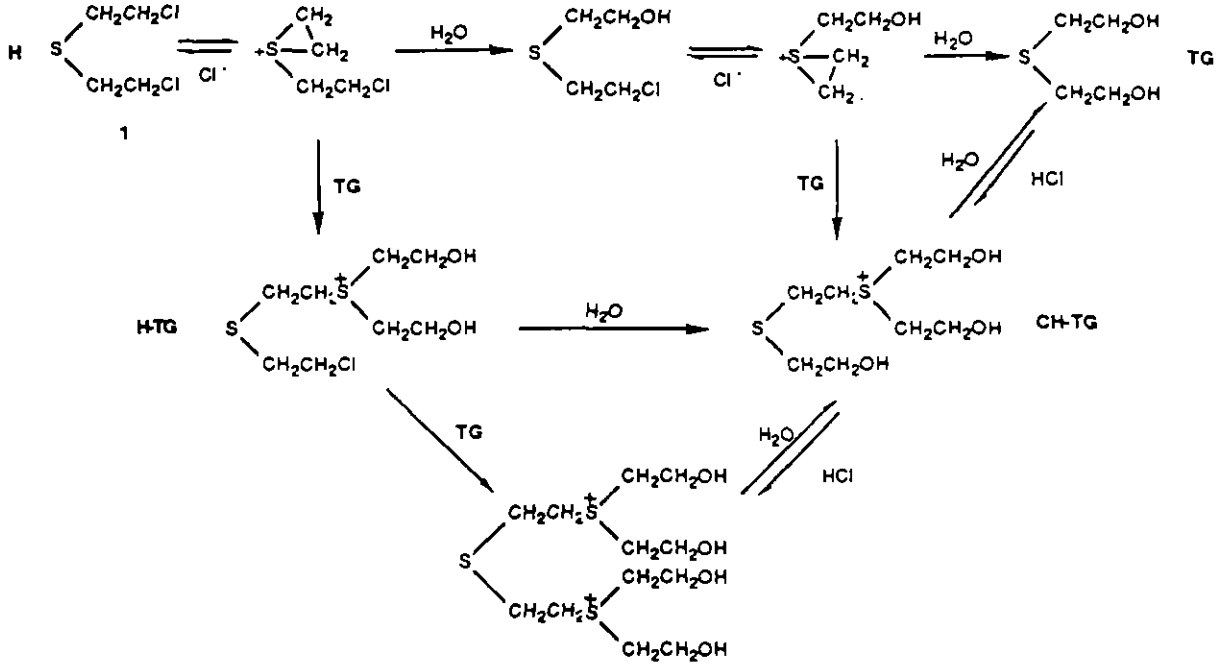
HD is insoluble in water, but can react with water at the interface to form a complicated set of ionic products (Scheme V) which then diffuse rapidly to the bulk water phase. The rate of HD dissolution is so slow that these ionic products are produced at the interface even before any HD is dissolved. This makes it virtually impossible to determine the HD solubility accurately. Furthermore, although HD has been reported to hydrolyze with a half-life of 5 min at 25 °C via an S_n1 mechanism,[18] HD cannot be detoxified by hydrolysis. The observed rate of HD hydrolysis is controlled by the rate of mass transfer and is, in fact, very slow. When a polar organic solvent is mixed with water to solubilize HD, the reduced polarity of the medium greatly reduces the S_n1 hydrolysis rate. Besides, the inhibition of HD hydrolysis by the chloride ion is significant,[18] and the rate of this ion pair return step also increases markedly as the solution becomes less polar.[21]

As shown in Scheme V, thiodiglycol (TG) is not the only product from HD hydrolysis. The sulfonium ion aggregates, H-TG, CH-TG, and H-2TG, are stable products in water at ambient temperatures, and H-TG is believed to be quite toxic.[22,23] The yields of these polymeric products increase as the initial concentration of HD increases.[21] Furthermore, TG and HCl, have been shown to react reversibly to form the same polymeric sulfonium ion intermediates.[21] The rate of this reverse reaction increases as the concentrations of both TG and HCl increase. Hence, despite the apparently rapid and irreversible hydrolysis of HD to TG in an infinitely dilute solution,[18] the hydrolysis of larger amounts of HD (~0.1 M) is a reversible process with the sulfonium ion aggregates as the predominant equilibrium species. These aggregates may, in part, account for the observed persistence of HD in the natural environment.

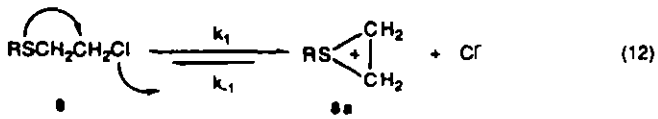
C. Nucleophile-Assisted Substitution of HD

A systematic investigation into the mechanisms of nucleophilic substitution of HD analogs was recently completed by a research group at the University of Alabama in Huntsville.[24] Using deuterated HD analogs such as $CH_3SCH_2CD_2OTs$ and $C_6H_5SCH_2CD_2Cl$, these researchers detected complete deuterium scrambling in the presence of a series of nucleophiles for almost all types of organic and aqueous solvent mixtures. Therefore, it can be concluded that the nucleophilic substitution of HD or its analogs proceeds, as predicted,

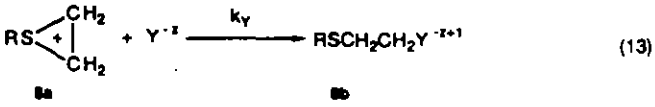
Scheme V. Reversible Formations of the Sulfonium Ion Aggregates in the Hydrolysis of Mustard (H)



exclusively via an S_n1 mechanism. The sulfur in these molecules is located at the best position to participate internally in the cleavage of the C–Cl bond by forming a transient cyclic ethylenesulfonium ion intermediate (**8a** in eq 12). Any external nucleophile Y (including water or another molecule of **8**, eq 13) cannot compete with the internal sulfur. Only one exception is reported: in pure dimethyl sulfoxide in the presence of thiophenolate anion, there was no scrambling of the isotopes and the substitution was, therefore, S_n2.[24c]



(12)



(13)

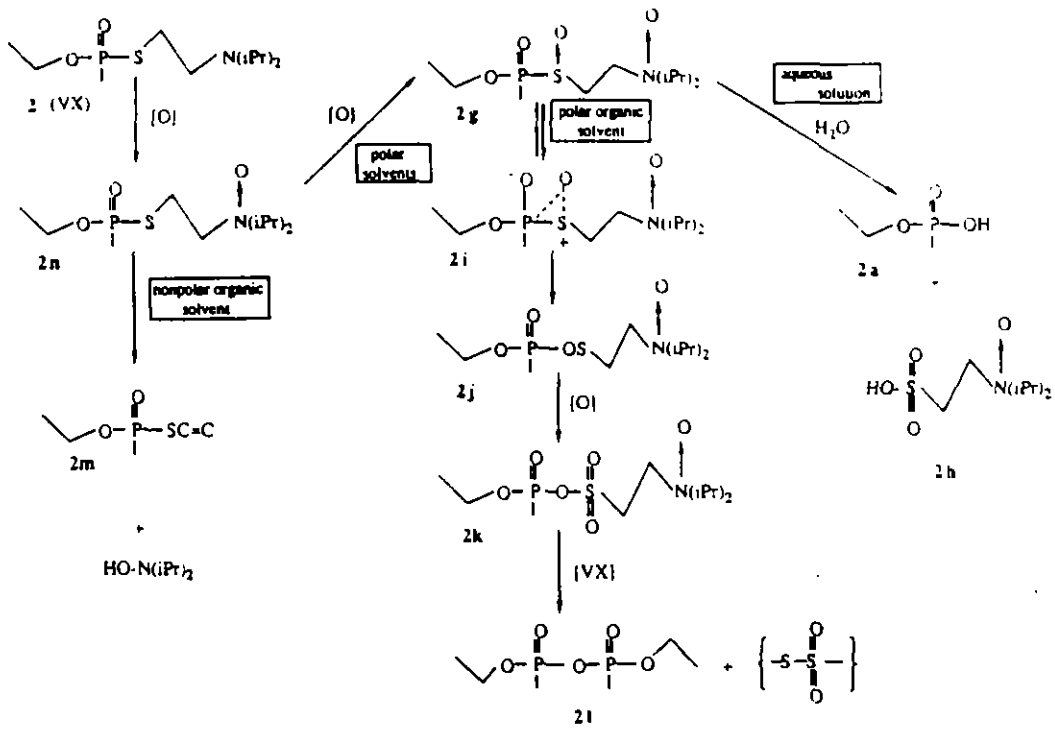
It is important to note that the observed rate of an S_n1 substitution reaction can increase in the presence of Y. This is not because of a mechanistic change but because of the competition between Y and the chloride ion as reflected in the relative magnitudes of (k_{-1}[Cl^-]) and (k_Y[Y]) (eqs 12 and 13).[25] Since the magnitude of k_Y[Y] increases with both the strength of the nucleophile and the concentration of Y, the observed rate enhancement by a nucleophile can be significant; and this enhancement may even be proportional to the concentration of Y. It is important that this rate behavior is not interpreted as an evidence for the S_n2 mechanism. Furthermore, such nucleophile-assisted substitution also reduces the formation of the stable sulfonium ion aggregates which may decompose to regenerate HD. Many such systems have been considered or recommended for the large-scale destruction of mustard. The nucleophiles proposed include amines and anions such as hydroxide, phenolate, and thiosulfate. Note that to achieve decontamination the final product (**8b**) must be nontoxic. In the presence of these nucleophiles, the reaction mechanism remains S_n1 and the rate-determining step (k_1 in eq 12) is controlled only by the solvent polarity.[21] The role of the nucleophile is 2-fold: to increase the observed rate by eliminating the return step and to eliminate the formation of the complicated products shown in Scheme V.

D. The Oxidation of HD and VX

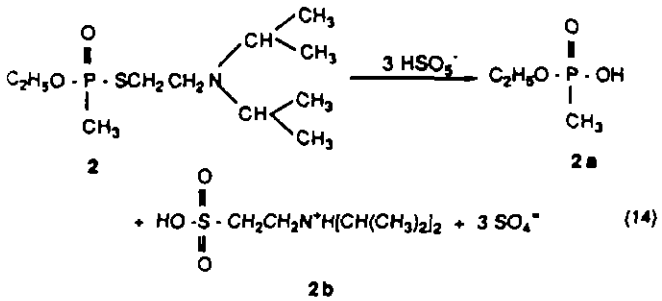
In aqueous solution, both HD and VX can be oxidatively detoxified. For a given oxidant, the sulfur in HD is oxidized at a much faster rate than the sulfur in VX. Once the sulfur in VX is oxidized, hydrolysis of the P–S bond occurs immediately to form **2a** and a sulfonic acid. Consequently, the *S*-oxide of VX (**2g** in Scheme VI) has never been identified in aqueous solution.[26] In acidic solution, the nitrogen in VX is protonated and not oxidized, whereas in basic and neutral solutions, the tertiary amine moiety is oxidized to the stable *N*-oxide more rapidly than the sulfur is oxidized. In those situations where only the nitrogen is oxidized for lack of either sufficient oxidant or a sufficiently strong oxidant to attack the sulfur, VX is not detoxified because the *N*-oxide product is still toxic.

The observed oxidation rates of both HD and VX by anionic oxidants decrease as the polarity of the solvent decreases. This is believed to be attributed to the S^+–O^- and N^+–O^- ion-pair complexes in the transition states.[26,27] In an anhydrous organic solvent, both the sulfur in HD and the nitrogen in VX can still be oxidized by strong oxidants at reasonable rates, although the rate of the sulfur oxidation in VX becomes extremely slow.[26] When the sulfur in the *N*-oxide is oxidized in an organic solvent, both the sulfonate **2k** and the toxic pyrophosphonate (anhydride **2l** in Scheme VI) are identified as the final products.[26] Based on a series of publications by Casida and co-workers,[28] Scheme VI

Scheme VI. *Multiple Paths in the Oxidation of VX in Neutral Solutions*



was proposed for the oxidation mechanism of VX in polar organic solvents. It is proposed that **2g** is formed first and slowly rearranges via the cyclic transition state **2i** to the sulfenate **2j**,[28] which is immediately oxidized to the sulfonate **2k**. In the absence of excess oxidant, **2k** reacts with another VX molecule to form **2l**. This reaction of the sulfonate with excess substrate in the absence of water to form the anhydride was carefully examined with a thioate pesticide.[29] In this study, the formation of an ion-pair intermediate which subsequently decomposed to the observed anhydride product was proposed as the most probable mechanism. In addition, a competing and parallel reaction to sulfur oxidation exists; the *N*-oxide (**2n**) can decompose to **2m** and the hydroxylamine via the Cope reaction at a rate dependent on the polarity of the organic solvent.[26] Compound **2m** may still be toxic and contains a sulfur atom more resistant to oxidation than that in VX. Therefore, VX cannot be rendered nontoxic by oxidation in the absence of water.



(14)

As a result of these studies, a number of oxidants containing peroxygen such as *m*-CPBA (*m*-chloroperoxybenzoic acid) and MMPP (magnesium monoperoxyphthalate) were found to be effective for both HD and VX. An aqueous solution of a commercial oxidant, Oxone (active component: $KHSO_5$),[26,30] was recommended for VX detoxification and for destruction of VX in laboratories at large scales (up to 51 g).[31] The aqueous solution of Oxone also acts as an acidic buffer (pH = 1.9) and can dissolve large amounts of VX followed by fast oxidation at the sulfur. Since the nitrogen is protonated, only 3 equiv of the oxidant are required for each equivalent of VX (eq 14).[26] This method is superior to the previous laboratory decontamination method which used excess bleach in an ethanol–water mixture at high pH.[12]

Since aqueous Oxone is a simple and effective decontaminant for VX, it was also investigated for the decontamination of HD and G agents. In a solution of 0.05 M mustard, 0.1 M Oxone, and 15 vol % *N*-methyl-2-pyrrolidinone (necessary to dissolve the mustard), HD is oxidized immediately to the sulfoxide which then converts completely to the sulfone in less than 1 h. Using fast kinetic techniques and UV absorption, an HD analog, $PhSCH_2CH_2Cl$, was found to oxidize with a half-life of 7 s at 25 °C in 0.002 M Oxone and 20 vol % CH_3CN.[27] As for GB and GD, neither oxidation nor displacement of the OR groups is observed in these Oxone solutions. Simple hydrolysis of the P–F bond to form the corresponding phosphonic acids **3a** and **4a** as shown in eq 1 is the exclusive hydrolysis pathway. The acid-catalyzed hydrolysis rate profiles for GB and GD at 18 °C are shown in Figure 2. These pseudo-first-order rates for 0.03 M GB and 0.02 M GD in the pH 2 buffer of 0.1 M Oxone are relatively slow. Therefore, Oxone is a superb decontaminant for both VX and HD but cannot rapidly detoxify the G agents.

IV. Decontamination Media

As discussed earlier, rapid dissolution of agents in the decontamination medium is essential to achieve effective decontamination (i.e., rapid removal of agent from surfaces). The decontamination media can be divided into liquid and solid systems. Liquid media can be further divided into nonaqueous (organic) and

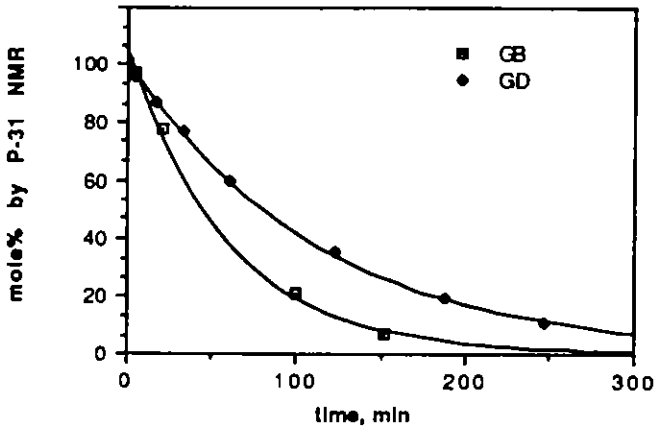


Figure 2. Hydrolysis of GB and GD in Oxone solutions at 18 °C.

aqueous media. Nonaqueous media such as DS2 offer good solubility for all agents but large amounts of organic waste are generated by the decontamination process. Aqueous media have the advantage of using water from natural resources. Soap solutions solubilize neat agents, but fail to dissolve the thickened agents; so an organic solvent is often added to the aqueous solution to improve dissolution. However, many of the oxidation and substitution reactions become slower as the solvent polarity decreases. The design of a decontamination medium is usually a compromise between solubility and optimum reactivity. Solid decontamination media have only been recently investigated. One property of these materials is the ability to absorb large amounts of liquid agents. Reactants incorporated in the solid support are usually less reactive than in a liquid solution. A few examples of these liquid and solid decontamination media are discussed below.

A. Heterogeneous Liquid Media

Since chemical agents are organic compounds of low polarity and most reactants (e.g., hydroxide ion, hypochlorite ion, and the anionic oxidants) are polar compounds, both micelles and emulsions have been investigated as potential liquid decontamination media. Of these systems, the best studied are the German emulsion (code name: C8)[32] and a microemulsion system MCBD (multi-purpose chemical, biological decontaminant).[33] In addition, a phase-transfer system was examined by Ramsden and his collaborators at the University of Florida.[34] In all of these systems, tetrachloroethylene was used as the organic phase and active chlorine was the reactant. Reactions take place at the surfaces of the droplets in both the C8 emulsion and the microemulsion (MCBD) systems. In the phase-transfer system, oxidation of sulfide takes place in tetrachloroethylene via transfer of the hypochlorite ion by the phase-transfer catalyst [$(nBu)_4N^+Cl^-$].

The German emulsion (C8) is composed, by weight, of 15% tetrachloroethylene (the continuous phase), 76% water, 1% anionic surfactant, and 8% $Ca(OCl)_2$. Because of the organic continuous phase, it is noncorrosive and as good a solvent as pure tetrachloroethylene for the thickened agents. In addition, C8 can penetrate into paint to dissolve and react with imbedded agent without damaging the paint. When the emulsion is sprayed, a thin, coherent film is formed on the surface to allow sufficient residence time for reaction with the agents.

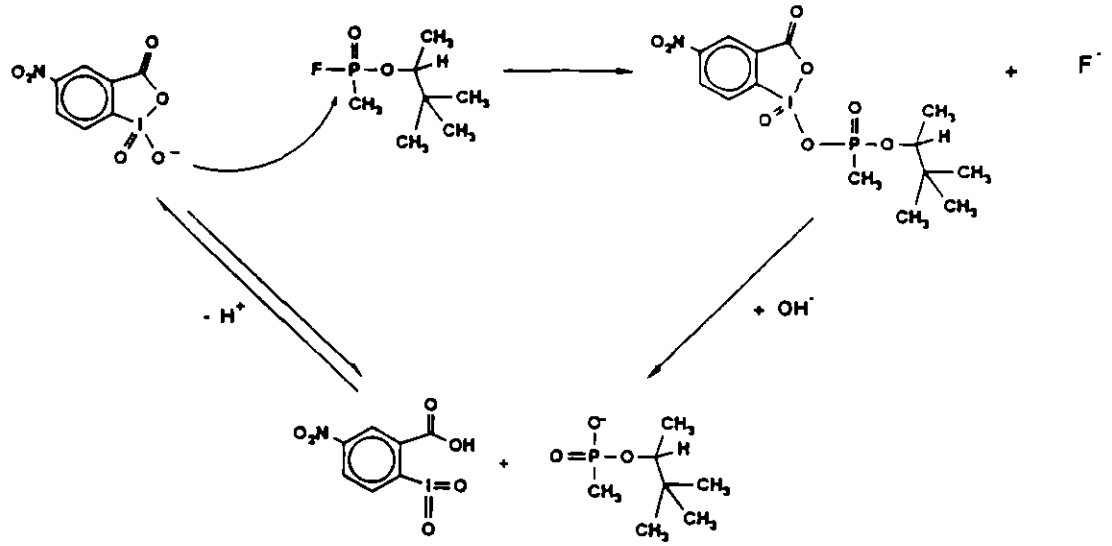
The microemulsion medium of the MCBD system is made, by weight, of 60% water (the continuous phase), 7% tetrachloroethylene, 28% CTAC (*n*-cetyl trimethylammonium chloride), and a small amount of a cosurfactant [$(nBu)_4NOH$]. To this microemulsion, 4% Fichlor, 0.1% sodium 2-nitro-4-iodoxybenzoate (IBX, see Scheme VII), and sodium borate are added for reactions with the agents. The MCBD system was designed to be superior to the C8 system because it is a more stable emulsion at a lower pH of 10, contains less tetrachloroethylene, and is partially catalytic. The catalysis by IBX, a derivative of *o*-iodosobenzoic acid (IBA), is proposed in Scheme VII, in which IBX is shown as a nucleophilic catalyst for the hydrolysis of GD.[35,36] Since the hydrolysis products are acidic, the borate buffer is essential to keep the IBX active. The IBX-catalyzed hydrolysis is significantly enhanced in cationic micelles in which both the IBX and the organic substrate are concentrated on the micellar surfaces. As a result, large rate enhancements have been observed for the more hydrophobic simulants such as PNPDPP but the hydrolyses of GB and GD, which are more polar, are only slightly accelerated.[36]

IBX was found to have little effect on the hydrolysis of VX. As shown in Figure 3, the hydrolysis of VX is catalyzed by IBX only in the initial stage of the reaction. After the first few minutes, deactivation of the catalyst is apparent in the rate profile. Perhaps the IBX, which is also an oxidant, is reduced by the thiol hydrolysis product (2e, eq 10) and cannot catalyze the reaction further. HD, as discussed above, is hydrolyzed via an S_n1 mechanism and, thus, cannot be catalyzed by IBX. Fichlor is added to the MCBD system to oxidize both HD and VX. Recently, Menger used a small amount of commercial bleach (5–6% NaOCl) to oxidize 2-chloroethyl ethyl sulfide in microemulsions (aqueous continuous phase) containing *tert*-butyl alcohol as the cosurfactant.[38] The oxidation was complete in 15 s and 2-chloroethyl ethyl sulfoxide was the only product. It was proposed that the hypochlorite ion was converted to *tert*-butyl hypochlorite at the droplet surfaces and reacted effectively with the HD simulant in the oil phase.

B. Polymer Powders and Supported Reagents

A solid sorbent system, the M291 kit, has recently been adopted for use as the primary skin decontaminant (see Table II). A sorbent decontaminant is a nontoxic, free-flowing, solid material which absorbs liquid agent tightly in its micropores. It is used by the soldier to wipe bulk liquid agent from his skin, clothing, and personal equipment. The major advantages of using a solid sorbent material for personal decontamination are its high capacity to absorb liquid chemical agents and the reduced weight of decontaminant that the soldier must carry compared to a liquid decontaminant of similar effectiveness. This new kit is composed of nonwoven fiber pads which are filled with a resin mixture (trade name: XE-555) developed by Rohm & Haas Company. The resins are made of a styrene-divinyl benzene copolymer and are composed of a high surface area carbonized macroreticular styrene/divi-

Scheme VII. Mechanism of IBX-Catalyzed Hydrolysis of GD



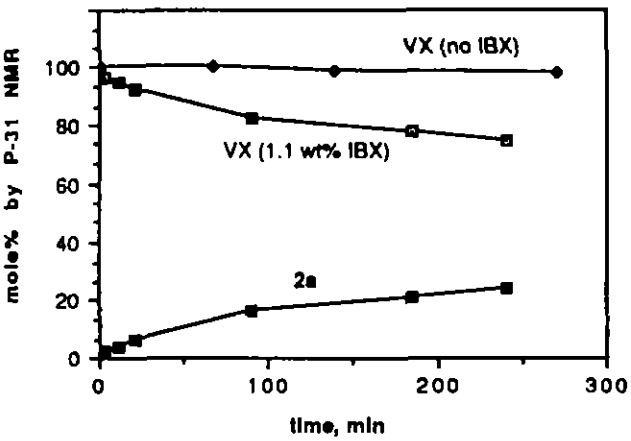


Figure 3. Hydrolysis of 0.1 M VX in a microemulsion at pH 10 and 18 °C.

nylbenzene resin (the sorptive resin), a strong acid (sulfonic acid groups) cation-exchange resin, and a strong base (tetralkylammonium hydroxide groups) anion-exchange resin. The sorptive resin can rapidly absorb liquid agents, and the reactive resins are intended to promote hydrolysis of the physisorbed agents. This resin blend was found to be less corrosive to the skin than the M258A1 system described earlier.

A recent NMR investigation of the XE-555 resin in the kit has provided the first direct evidence for agent–resin interactions.[39] The study showed that neither VX nor $^{13}CH_3SCH_2CH_2Cl$ (HD simulant) hydrolyzed on the resin surface during the first 10 days of observation. GD slowly hydrolyzed with a half-life of about 30 h. It appears that the observed rapid agent removal in field practice is achieved physically by wiping with the pad and presumably by a simultaneous physisorption of the agent on the sorptive resin component. For reasons discussed previously, it is not surprising that no hydrolysis was measured for either HD or VX. On the other hand, GD was expected to hydrolyze quickly on the basic sites of the reactive resin component. It is therefore postulated that most of the GD is absorbed on the sorptive resin sites and does not rapidly migrate to the basic sites of the reactive resin. These results demonstrate that reactions on solids are controlled by a different set of variables than those in liquid solutions. For solid decontamination materials, the sorption and physical removal processes are perhaps far more effective than any chemical reactions.

V. Applications of Catalysis to Decontamination

A. Metal Ion Catalyzed Hydrolysis

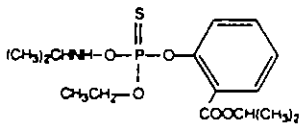
The ability of copper(II) to catalyze the hydrolysis of the G agent simulant, DFP, was first demonstrated by Warner-Jauregg and co-workers in 1955.[40] Later, Martell et al. extended the study to GB and screened the activity of a number of other metal ions.[10b,41] The authors concluded that copper(II), in particular, was a potent catalyst for the hydrolysis of GB. The rate law for the catalysis is shown to be first-order in hydroxide ion, metal ion, and GB. The observed first-order rate coefficient for metal ion catalyzed hydrolysis is shown in eq 15 where k_{hyd} is the spontaneous (noncatalytic) hydrolysis rate and is very small compared with k_2.

$$k_{obs} = k_{hyd} + k_2[OH][Cu^{+2}] \qquad (15)$$

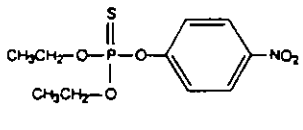
Two mechanisms for the activation step are possible. The catalytic species could be the hydroxometal complex $CuOH^+$, or Cu(II) could act as a Lewis acid by complexing with the substrate at the phosphoryl oxygen followed by attack of the hydroxide ion on the GB–Cu complex.[42] These findings generated a great deal of interest in subsequent studies attempting to verify the mechanism.[43,44]

The copper(II)-catalyzed hydrolysis of GD in a pH 7 buffer was not investigated until the 1980s.[45] As in the case of GB, the rate of GD hydrolysis is accelerated by 1 order of magnitude in the presence of 0.001 M $CuSO_4$ at 25 °C. When $CuSO_4$ is increased to 0.01 M, the reaction becomes too fast to be followed under the same conditions. Only limited Cu(II)-catalyzed hydrolysis was examined with VX. It is speculated that the diisopropylamino group of VX may be a competing site for complexing with copper; thus, the reaction may be inhibited. Because of the S_n1 nature of HD reactions via neighboring group participation, the hydrolysis of HD is expected to be inhibited if Cu(II) complexes with the sulfur. Other metal ions, such as Ag^+ and Hg^{2+}

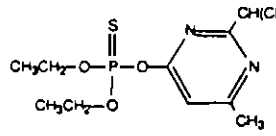
Scheme VIII. Structures of Pesticides



Isophenfos



Parathion



Diazinon

appeared to accelerate HD hydrolysis by complexing with the chloride ion. However, these ions cannot be applied to decontamination because Ag^+ is expensive and Hg^{2+} is toxic.

B. Enzymatic Decontamination and Biodegradation

1. Enzymatic Hydrolysis of Nerve Agents

In 1946, Mazur reported the first work concerned with enzymes capable of catalytically hydrolyzing organophosphorus esters.[46,47] During the 1950s and 60s, a number of groups investigated the hydrolysis of GB, DFP, and paraoxon (Scheme VIII), by enzymes from a variety of organisms (primarily mammalian tissues and bacteria).[48] A result of the increased interest in these enzymes was the proliferation of names for them. The literature is filled with references to enzymes such as DFPase, fluorophosphatase, phosphorylphosphatase, paraoxonase, phosphofluorase, phosphotriesterase, sarinase, somanase, and tabunase. In 1987, the name organophosphorus acid (OPA) anhydrase was selected as a generic name for all enzymes that are capable of catalytically hydrolyzing organophosphorus compounds of interest.

Hoskin began his research into the purification and characterization of the OPA anhydrase from squid in 1966.[49-52] The significance of the squid enzyme lies in the fact that it has major differences from all the other OPA anhydrases. The differences were great enough that in 1984 Hoskin proposed that the enzymes could be grouped into two categories, the squid-type (for which there was one example) and all others, which were referred to as Mazur-type.[53] A summary of the properties of these enzyme types is shown in Table III.[53] Because of the types of enzymes (particularly bacterial) that have been isolated and characterized within the past 10 years, these categories are no longer as simple as originally believed.

The interest in microbial enzymes for the degradation of organophosphorus compounds received a boost in the early 1970s with the isolation of bacteria capable of growing on pesticides such as diazinon, isophenfos, and parathion (Scheme VIII).[54-56] By far, the most studied bacterial enzyme is parathion hydrolase. An essentially identical enzyme has been found in *Pseudomonas diminuta* and a *Flavobacterium* species (ATCC 27551).[57] The gene for the enzyme has been cloned and sequenced and the reaction mechanism determined.[58] Parathion hydrolase has a broad substrate range with the organophosphorus pesticides,[59] but much lower activity on the chemical agents.[60]

Table III. Properties of Organophosphorus Acid Anhydrases

squid-type	Mazur-type
narrow distribution, squid nerve, saliva, hepatopancreas	Ubiquitous
molecular weight, 30–38 000	variable, 45–90 000
GD/DFP ≈ 0.25	GD/DFP, 5–50 and higher
hydrolyzes all isomers of soman; some stereoselectivity in rates	stereoselectivity variable: often quite stereospecific
Mn^{2+} indifferent or slightly inhibited	Mn^{2+} stimulated 2–20-fold and as high as 80-fold
Ca^{2+} requiring, not Ca^{2+} stimulated	May be Mg^{2+} requiring and stimulated
$(NH_4)_2SO_4$ indifferent	$(NH_4)_2SO_4$ labile
Mipafox ($[CH_3)_2N]_2P(O)F$) indifferent	Mipafox inhibited

Table IV. Comparison of Several OPA Anhydrases

	specific activity (μmol min^{-1} mg^{-1})		
enzyme	DFP	GD	paraoxon
parathion hydrolase	60	5	3200
squid hepatopancreas	300	60	
Alteromonas sp. JD6.5	300	600	12

Only two other OPA anhydrases have been purified to homogeneity and characterized. These are the squid hepatopancreas enzyme and an enzyme from a halophilic bacterial isolate tentatively identified as a strain of *Alteromonas*.[61] It is important to note that these enzymes are active for all of the optical isomers of the G agents. A comparison of these three enzymes with regard to their specific activity for DFP, GD, and paraoxon is shown in Table IV.[62] Although the halophile enzyme has by far the greatest activity, other properties such as pH, temperature optima, stability, and potential inhibitors could play an important role in the selection of enzymes for decontamination formulations. In addition, enzymes from other sources continue to be examined and may offer even greater activity and substrate range.

2. Cloning of OPA Anhydrase Genes

For enzymes to achieve a substantial impact on the development of a new generation of decontamination systems, they will need to be producible in large quantities. With the advent of genetic engineering, the prospect of bacteria and other easily cultured organisms being used as microfactories for the production of rare or important proteins has become a reality.

The OPA anhydrase from *Pseudomonas diminuta* MG and *Flavobacterium* sp. is coded for by a plasmid-borne gene (opd) of 1079 base pairs in length which is identical in both organisms even though their plasmids are totally different.[57] Recent work has focused on the overexpression of the opd gene product in better host systems. The results show that the production of mature enzyme could be achieved in *Escherichia coli*,[62] *Drosophila melanogaster*,[63] *Streptomyces lividans*,[64] and Fall Armyworm.[65] The lack of significant activity of parathion hydrolase on GD would indicate that this enzyme is not as well suited for decontamination of the nerve agents as are some other enzymes. However, it continues to serve as an excellent model enzyme system

Table V. Summary of ^{13}C NMR Profile of Hydrolyzed and Biodegraded Mustard

strain	% original carbon remaining	compounds detected
SH18	16	thiodiglycol sulfoxide
SH42	2–3	thiodiglycol, thiodiglycol sulfoxide, small amounts of ethers or thioethers

The OPA anhydrase from *Alteromonas* sp. JD6.5 currently demonstrates the highest activity against GD. The enzyme is a single polypeptide with a molecular weight of 60 000 Da.[61] Recently, the gene that codes for this enzyme has been cloned into *E. coli* with the Lambda ZAP expression vector.[66] Using polyclonal and monoclonal antibodies and an oligonucleotide probe derived from the partial N-terminal sequence of the JD6.5 enzyme, positive clones have been identified and purified. The OPA anhydrase gene has been found to reside within a 4 kilobase KpnI DNA fragment. Western blot analysis has indicated that the OPA anhydrase is expressed in *E. coli* and that the expressed product is enzymatically active. Efforts are now underway to sequence the cloned gene.

The third enzyme for which cloning studies are underway is the squid OPA anhydrase. While there are some variations between species of squid, the enzymes are very similar in molecular weight (30–38 000 Da). Recently, Kopec-Smyth et al.[67] constructed a cDNA library derived from squid hepatopancreas tissue in *E. coli* using the expression vector pcDNAII. One positive clone was detected through the use of polyclonal and monoclonal antibodies and two oligonucleotide probes derived from the partial N-terminal sequence of the enzyme. Preliminary data suggest that the clone contains approximately 75% of the total gene coding sequence. In addition, Lunzer et al.[68] examined an enzyme from squid optic ganglion and found that the N-terminal amino acid was blocked. These investigators also have prepared a cDNA library in the Lambda ZAP system. In order to gain further understanding of the enzyme structure, both groups are now preparing to sequence the cloned genes.

3. Biodegradation of HD

In an attempt to achieve the biodegradation of HD, soil samples were collected from areas purported to have previously been contaminated by HD. Enrichment cultures were set up with bacteria from these samples using thiodiglycol as the sole carbon source in a mineral salts medium. Two bacterial strains were isolated which utilize thiodiglycol as their sole source of carbon for growth.[69] As shown in Table V, these strains were designated SH18 and SH42 and were identified as *Pseudomonas pickettii* (37.5% fatty acid identity) and *Alcaligenes xylosoxidans* ssp. *xylosoxidans* (74.1% fatty acid identity), respectively.

Initial attempts to grow these organisms on HD proved to be unsuccessful since the organisms were killed by HD in culture. However, subsequent efforts in which the HD was shaken in mineral salts medium overnight prior to inoculation proved successful. Under these conditions, both strains of bacteria were able to utilize the hydrolyzed HD as their sole source of carbon for growth. Bacteria were grown from a single colony inoculum in mineral medium with hydrolyzed HD provided as the sole carbon source. Growth was allowed to proceed into the stationary phase for a total of 260 h. Doubling time for the cultures was approximately 10 h for strain SH18 and 40 h for strain SH42 (see Table V). ^{13}C FTNMR analysis was performed before inoculation and after growth. The cell mass was not removed during the analysis. As shown in Table V, the NMR results showed that the bacteria had degraded as much as 97% of the carbon-containing compounds in the medium. Mineralization was demonstrated by the evolution of $^{14}CO_2$ from the culture. Two different microtoxicological tests detected no toxicity in the resulting medium. Currently, efforts are underway to determine the feasibility of HD biodegradation in a pilot scale system and to conduct more extensive toxicological tests on the resulting products.

C. Catalytic Oxidation

One approach to catalytic decontamination is to activate the oxygen in air for the oxidation of both HD and VX. Although such catalysts in the form of organometallic complexes do exist,[70] the concentration of oxygen in air at ambient conditions is too low for the large amount of substrate encountered in decontamination. A number of studies using hydrogen peroxide (H_2O_2) as the model oxidant and metal ions as the catalysts have also been conducted. The oxidation of HD by H_2O_2 is slow in the absence of a catalyst. At 21 °C in an equal-volume binary solvent mixture of water and *N*-cyclohexyl-2-pyrrolidinone, the observed reaction half-life of HD with 1% H_2O_2 is 6 h, and the HD sulfoxide is the only product. This reaction could be catalyzed using a $V(O)(acac)_2$ complex (acac = $CH_3C(O)CH_2C(O)CH_3$) prepared by Drago and co-workers.[71] In CH_3CN, at 0.1 M $CH_3SCH_2CH_2Cl$, 0.01 M $V(O)(acac)_2$, and 1 M H_2O_2, all of the sulfide substrate was converted to the sulfoxide in less than 2 min at 20 °C. However, this system is not effective for the VX analog **9** (eq 11). A series of catalysts containing iron were also studied in order to examine if Fenton type chemistry[72] could be used to oxidize both VX and HD via the formation of the hydroxyl radical (•OH) as the reactive species. None of the iron catalysts tested to date are effective for either HD or VX. One reason for the lack of oxidation was the decomposition of the peroxide by the iron catalysts forming molecular oxygen, which then escaped from the reaction mixture, and deactivated the catalyst. Work in this area is continuing, since metal ions and complexes are known to be excellent oxidation catalysts. Additionally, stable oxidants need to be identified and tested against agents under decontamination conditions.

The application of a photocatalyst in the air oxidation of HD and VX has also been investigated.[73] Both VX and HD can be oxidized on irradiated TiO_2 surfaces in acetonitrile. A series of oxides and disulfides are produced from the photooxidation of mustard. However, the observed quantum yields of these reactions were low, in the 0.1–0.3% range.[74] In the absence of water, VX is primarily converted to the toxic pyrophosphate products (e.g. **21** in Scheme VI).[73b] When water is added to the solvent, nontoxic phosphonic and sulfonic acids are produced, although the solubility of air decreased in the aqueous solutions.

VI. Future Directions

Looking forward to the next century, the highest research priority in reactive decontamination is to identify both liquid and solid decontaminants which do not have adverse effects on the environment. The biodegradable *N*-alkyl-2-pyrrolidinones are being considered as the major organic components for new liquid decontaminants since these pyrrolidinones can penetrate into the thickeners.[75] Decontamination efficacy tests indicated that 4 wt % $Ca(OCl)_2$ in an equal volume mixture of *N*-cyclohexyl-2-pyrrolidinone and water can effectively detoxify the four agents.[76] In addition, preliminary data also indicate that the four agents can be detoxified by a strong base (alkoxide) in *N*-ethyl-2-pyrrolidinone in the same manner as DS2.

To develop noncorrosive decontamination systems, the search for catalysts (including enzymes) will continue. Of particular interest are those catalysts that are pH independent and those that can catalyze the oxidation of the OR groups in the G agents as well. Compared to liquid decontaminants, very little is known concerning the interaction of agents with solid decontaminants. In order to develop better solid decontamination materials, NMR imaging and magic-angle spinning (MAS) techniques will be applied to investigate the adsorption, site-exchange, and reaction characteristics of agents on solid matrices. Recently, advances in computational chemistry and access to supercomputers have opened the possibilities of predicting, modeling, and screening both liquid and solid decontamination systems containing enzymes and other types of catalysts. Finally, many of the decontamination research findings may be applied to the safe destruction of chemical weapons.[77] The Army currently incinerates the chemical agents but is also considering alternatives such as detoxification (neutralization) technologies.[78] These neutralization methods are being evaluated by a committee organized by the National Academy of Science, and their recommendations may influence future directions in the development of new decontamination systems.

Acknowledgments. The authors are deeply grateful for the contributions from Drs. T.-c. Cheng, Joseph. J. DeFrank, and Steven P. Harvey to the Section on Enzymatic Decontamination and Biodegradation and for the helpful discussions with Mrs. Linda L. Szafraniec, Mr. William T. Beaudry, and Mr. Joseph W. Hovanec.

References

(1) A range of surfaces are substrates for decontamination. These surfaces include the painted metal of large equipment such as the exteriors of tanks, ships, and aircraft; smaller personal equipment such as helmets, weapons, portable electronic devices, and protective clothing; and human skin.

(2) Most military equipment is painted with low-gloss paint. Agent penetration into paints has been observed. In the United States, a chemical agent resistant paint was developed and used to prevent penetration. In other NATO countries, sorptive paints are still used. For details, see: (a) Thompson, J. H.; Schwartz, M. Evaluation of the Resistance of Standard Air Force Paint to Liquid Toxic Agent Sorption. ARCSL-TM-79016, 1979. (b) Thompson, J. H.; Day, S. E.; Schwartz, M.; Keck, C. H. *Development of a Chemical Agent Resistant Coating*: ARCSL-TM-80017, 1980.

(3) For a review of chemical warfare agents and their properties, see: Compton, J. A. F. *Military Chemical and Biological Agents, Chemical and Toxicological Properties*. The Telford Press: Caldwell, N. [illegible] 1987.

(4) Papirmeister, B.; Feister, A. J.; Robinson, S. I.; Ford, R. D. *Medical Defense Against Mustard Gas: Toxic Mechanisms and Pharmacological Implications*; CRC Press, Inc.: Boca Raton, FL, 1991.

(5) For a review of the isolations and toxicities of the stereoisomers, see: Benschop, H. P.; de Jong, L. P. A. *Acc. Chem. Res.* **1988**, *21*, 368–374.

(6) The purpose of the thickener is to control the rheology of the agents as they are explosively disseminated from a munition. A typical thickener is Acryloid K125, a copolymer composed of methyl, ethyl, and butyl methacrylates produced by Rohm & Haas, Co. In addition, a polychlorinated isoprene has also been used as a thickener.

(7) McWilliams, J. L.; Steel, R. J. *Gas! The Battle for Ypres, 1915*; Vanwell Publishing Limited: Deyell Co., Canada, 1985.

(8) Fire has been observed when a significant quantity of HD comes in contact with HTH or STB powder.

(9) In most published work, only the oxidation products were reported for the reaction of HD and hypochlorite. Elimination products were detected only recently using both MS and ^{13}C and ^{1}H NMR. See: (a) Harris, J. M.; Pailey, M. S.; Sedaghat-Herati, M. R.; McManus, S. P. *J. Org. Chem.* **1985**, *50*, 5230. (b) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Davis, F. A. On Simulating the Oxidation Reactivities of HD and VX. In *Proceedings of the 1988 U.S. Army CRDEC Scientific Conference on Chemical Defense Research*, CRDEC-SP-013, U.S. Army CRDEC: Aberdeen Proving Ground, MD, August 1989; Vol. I.

(10) The half-life for GD hydrolysis at pH = 10 and 25 °C is 12 min at an ionic strength of 0.01 M $LiClO_3$ in the absence of any buffer. GB hydrolyzes faster than GD under identical conditions. For rate dependence on pH, see: (a) Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1962**, *84*, 2309–2316 (for GB); (b) Ward, J. R.; Yang, Y.-C.; Wilson, R. B., Jr.; Burrows, W. D.; Ackerman, L. L. *Bioorg. Chem.* **1988**, *16*, 12–16 (for GD).

(11) The hypochlorite anion was reported to catalyze the hydrolysis of GB by complexing with the phosphoryl group. See: Epstein, J.; Bauer, V. E.; Saxe, M.; Demek, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 4068–4071.

(12) NMR studies conducted by Szafraniec and Beaudry showed that VX could only be converted to the ethyl methylphosphonic acid (**2a** in eq 2) by a large excess of active chlorine in the basic hypochlorite solutions. The structures of the non-phosphorus products could not be completely identified. Sulfoxides, sulfones, and carboxyl compounds appeared to be present.

(13) (a) Jackson, J. B. *Development of Decontamination Solution DS2*; CWLR, 2368, April, 1960. (b) Richardson, G. A. *Development of a Package Decontamination System*; EACR-1310-17, Final Report, Contract DAAA15-71-C-0508, August, 1972.

(14) (a) Beaudry, W. T.; Szafraniec, L. L.; Leslie, D. R. Reactions of CW Agents in DS2. In *Proceedings of the 1990 CRDEC Scientific Conference on Chemical Defense Research*; CRDEC: Aberdeen Proving Ground, MD, November, 1990. (b) Beaudry, W. T.; Szafraniec, L. L.; Leslie, D. R. *Reactions of Chemical Warfare Agents with DS2*. Product Identification by NMR. I. Organophosphorus Compounds. CRDEC-TR-364, June, 1992.

(15) The Soviet kit contains a number of items: (1) a solution of NaOH, ethanol, and phenol in a plastic ampule; (2) a glass ampule containing solid chloramine-B powder; the glass ampule is contained in a larger plastic ampule filled with a solution of ethanol and dissolved $ZnCl_2$; (3) a vial containing tablets for internal use; (4) a glass ampule containing ammonium nitrate solution; (5) two syringes containing antidotes for GD; and (6) wooden stick scrapers to remove the thickened agents. Items 1 and 2 are identical to the M258 kit.

(16) (a) Szafraniec, L. L.; Beaudry, W. T., Ward, J. R.; Rohrbaugh, D. K. *Reactions Between Chemical Agents and the Chemicals in the M280 Decontamination Kit*; CRDEC-TR-134, CRDEC: Aberdeen Proving Ground, MD January, 1990. (b) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Ward, J. R. The Reaction of VX with Chloramine-B. In *Proceedings of the 1991 U.S. Army CRDEC Scientific Conference on Chemical Defense Research*; U.S. Army CRDEC: Aberdeen Proving Ground, MD, in press.

(17) (a) For the chemistry of chloramine-B, see: Campbell, M. M.; Johnson, G. *Chem. Rev.* **1978**, *78*, 65–79. (b) For reaction with sulfides, see: Ruff, F.; Kucsman, A. *J. Chem. Soc., Perkin Trans 2* **1975**, 509. For reactions with phosphorus-sulfur compounds, see: (c) Cadogan, J. I. G.; Moulden, H. N. *J. Chem. Soc.* **1961** 5524–5531. (d) Lakshminarayana, V. *J. Agric. Food Chem.* **1966**, *14*, 55–56.

(18) Bartlett, P. D.; Swain, C. G. *J. Am. Chem. Soc.* **1949**, *71*, 1406–1415.

(19) In concentrated solutions, reverse reactions become more competitive after sufficient products are accumulated. It usually takes much longer for the reaction to reach completion. More complicated reaction mechanisms such as aggregation of the substrate as well as disproportionation reactions are more likely to occur in more concentrated solutions. There is also the problem with mixing and solubilization of large amounts of the substrate.

(20) (a) Epstein, J.; Callahan, J. J.; Bauer, V. E. *Phosphorus* **1974**, *4*, 157–163. (b) Szafraniec, L. L.; Szafraniec, L. J.; Beaudry, W. T.

Ward, J. R. *On the Stoichiometry of Phosphonothiolate Ester Hydrolysis*; CRDEC-TR-212, July 1990.
(21) (a) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Ward, J. R. *J. Org. Chem.* **1988**, *53*, 3293–3297. (b) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Ward, J. R. *J. Org. Chem.* **1986**, *51*, 2756–2759.
(22) Steam has been used to decontaminate chemical agents on heat-resistant surfaces. Both the solubility and the rate of hydrolysis of agent increase at elevated temperatures. In addition, the sulfonium ion aggregates shown in Scheme V decompose at high temperatures. Although the toxic product **2f** from the hydrolysis of VX is expected, it may decompose at high temperatures.
(23) Anslow, W. P., Jr.; Karnofsky, D. A.; Val Jager, B.; Smith, H. W. *J. Pharmacol. Exp. Therap.* **1948**, *93*, 1–9.
(24) (a) McManus, S. P.; Neamati-Mazraeh, N.; Hovanes, B. A.; Paley, M. S.; Harris, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 3393–3395. (b) McManus, S. P.; Neamati-Mazraeh, N.; Karaman, R. M.; Harris, J. M. *J. Org. Chem.* **1986**, *51*, 4876. (c) Sedaghat-Herati, M. R.; McManus, S. P.; Harris, J. M. *J. Org. Chem.* **1988**, *53*, 2539–2543.
(25) The competition factors (k_Y/k_W) for a large number of nucleophiles reacting with the 2-chloroethyl ethylenesulfonium ion were reported by Ogston et al.: Ogston, A. G.; Holiday, R. E.; Philpot, J. St. L.; Stochen, L. A. *Trans. Faraday Soc.* **1948**, *44*, 45–52. Thiosulfate anion had a value of 27 000 M^{-1} and was among the most competitive nucleophiles. The value for the chloride ion was reported to be 20 M^{-1}.
(26) Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Rohrbaugh, D. K. *J. Am. Chem. Soc.* **1990**, *112*, 6621–6627.
(27) (a) Bacaloglu, R.; Blasko, A.; Bunton, C. A.; Foroudian, H. J. *Phys. Org. Chem.* **1992**, *5*, 171–178. (b) 2-Chloroethyl phenyl sulfide was found to oxidize at about the same rate as HD in a separate study: see: Yang, Y.-C.; Szafraniec, L. L.; Beaudry, W. T.; Davis, F. A. *J. Org. Chem.* **1990**, *55*, 3664–3666.
(28) In a series of papers by Casida and co-workers, the oxidation of phosphorothiolate and thioate pesticides was investigated in both protic and aprotic organic solvents. The equivalent of **2i** in Scheme VI was identified at −50 °C by NMR; therefore, **2i**, although short-lived, is in reality an intermediate. See: (a) Bellet, E. M.; Casida, J. E. *J. Agric. Food Chem.* **1974**, *22*, 207–211. (b) Segall, Y.; Casida, J. E. *Tetrahedron Lett.* **1982**, *23*, 139–142. (c) Segall, Y.; Casida, J. E. *Phosphorus Sulfur* **1983**, *18*, 209–212. (d) Bielawski, J.; Casida, J. E. *J. Agric. Food Chem.* **1988**, *36*, 610–615.
(29) Leslie, D. R.; Beaudry, W. T.; Szafraniec, L. L.; Rohrbaugh, D. K. *J. Org. Chem.* **1991**, *56*, 3459–3462.
(30) Professor Clifford A. Bunton of the University of California at Santa Barbara first suggested oxone to oxidize VX in 1988 (personal communication).
(31) Samuel, J. B. Personal communication, 1990–1991. Both the toxicity study of the waste solutions of VX in Oxone and the decontamination study of up to 51 g of VX by Oxone are soon to be published as two separate CRDEC technical reports.
(32) Ford, M. S.; Newton, W. E. *International Material Evaluation of the German C8 Emulsion*; DPG-FR-88-009, U.S. Army Dugway Proving Ground: Dugway, UT, March, 1989.
(33) J. W. Hovanec is the principle inventor of the MCBD system. Personal communication, 1988–1990.
(34) Ramsden, J. H.; Drago, R. S.; Riley, R. *J. Am. Chem. Soc.* **1989**, *111*, 3958–3961.
(35) Professor Robert A. Moss at Rutgers, the State University of New Jersey, is a pioneer in the study of *o*-iodosobenzoic acid (IBA) derivatives as catalysts for the hydrolysis of organophosphorus esters. See: (a) Moss, R. A.; Alwis, K. W.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1983**, *105*, 681–682. (b) Moss, R. A.; Alwis, K. W.; Shin, J.-S. *J. Am. Chem. Soc.* **1984**, *106*, 2651–2655. (c) Moss, R. A.; Kim, K. Y.; Swarup, S. *J. Am. Chem. Soc.* **1986**, *108*, 788.
(36) For the synthesis and activity of IBX, see: Katritzky, A. R.; Duell, B. L.; Durst, H. D.; Knier, B. L. *J. Org. Chem.* **1988**, *53*, 3972.
(37) Leslie, D. R.; Pantelidis, S. *Aust. J. Chem.* **1990**, *43*, 937–743.
(38) Menger, F. M.; Elrington, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 9621–9624.
(39) Leslie, D. R.; Beaudry, W. T.; Szafraniec, L. L. *Sorption and Reaction of Chemical Agents by a Mixed Sorbtive/Reactive Resin*; CRDEC-TR-292, CRDEC: Aberdeen Proving Ground, MD, Oct. 1991.
(40) Wagner-Jauregg, T.; Hackley, B. E.; Lies, T. A.; Owen, O. O.; Proper, R. *J. Am. Chem. Soc.* **1955**, *77*, 922.
(41) (a) Gustafson, R. L.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 525. (b) Gustafson, R. L.; Chabarek, S.; Martell, A. E. *J. Am. Chem. Soc.* **1963**, *85*, 598.
(42) Epstein, J.; Rosenblatt, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 3596.
(43) Fowkes, F. M.; Ronay, G. S.; Ryland, L. B. *J. Phys. Chem.* **1958**, *62*, 867.
(44) Ward, J. R.; Szafraniec, L. L.; Beaudry, W. T.; Hovanec, J. W. *J. Mol. Catal.* **1990**, *58*, 373.
(45) Ward, J. R.; Hovanec, J. W.; Albizo, J. M.; Szafraniec, L. L.; Beaudry, W. T. *Fluorine Chem.* **1991**, *51*, 277.
(46) Mazur, A. *J. Biol. Chem.* **1946**, *164*, 271–289.
(47) McCombie, H.; Saunders, B. C. *Nature (London)* **1946**, *157*, 287–289.
(48) For a review, see: Mounter, L. A. Metabolism of organophosphorus anticholinesterase agents. In *Handbuch de Experimentellen Pharmakologie: Cholinesterase and Anticholinesterase Agents*; Kolle, G. B., Ed., Springer-Verlag: Berlin, 1963; pp 486–504.
(49) Hoskin, F. C. G.; Rosenberg, P.; Brzin, M. Re-examination of the effect of DFP on electrical and cholinesterase activity of squid giant nerve axon. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *55*, 1231–1235.
(50) Hoskin, F. C. G. *Science* **1971**, *172*, 1243–1245.
(51) Hoskin, F. C. G.; Long, R. J. *Arch. Biochem. Biophys.* **1972**, *150*, 548–555.
(52) Hoskin, F. C. G.; Roush, A. H. *Science* **1982**, *215*, 1255–1257.
(53) Hoskin, F. C. G.; Kirkish, M. A.; Steinmann, K. E. *Tox. Appl. Pharmacol.* **1984**, *4*, S165–172.
(54) Sethunathan, N.; Yoshida, T. *Can. J. Microbiol.* **1973**, *19*, 873–875.
(55) Racke, K. D.; Coats, J. R. *J. Agric. Food Chem.* **1987**, *35*, 94–99.
(56) Siddaramappa, R.; Rajaram, K. P.; Sethunathan, N. *Appl. Microbiol.* **1973**, *26*, 846–849.
(57) Harper, L. L.; McDaniel, C. S.; Miller, C. E.; Wild, J. R. *Appl. Environ. Microbiol.* **1988**, *54*, 2586–2589.
(58) Lewis, V. E.; Donarski, W. J.; Wild, J. R.; Raushel, F. M. *Biochemistry* **1988**, *27*, 1591–1597.
(59) Munnecke, D. M. *J. Agric. Food Chem.* **1980**, *28*, 105–111.
(60) For a review, see: DeFrank, J. J. Organophosphorus Cholinesterase Inhibitors: Detoxification by Microbial Enzymes. In *Applications of Enzymes Biochemistry*; Kelly, J. W., Baldwin, T. O., Ed.; Plenum Press: New York, 1991.
(61) DeFrank, J. J.; Cheng, T.-c. *J. Bacteriol.* **1991**, *17*, 1938–1943.
(62) (a) Dumas, D. P.; Durst, H. D.; Landis, W. G.; Raushel, F. M.; Wild, J. R. *Arch. Biochem. Biophys.* **1990**, *277*, 155–159. (b) Sedar, C. M.; Murddock, D. C.; Rohde, M. F. *Bio/Technology* **1989**, *71*, 151–1155.
(63) Phillips, J. P.; Xin, J.; Kirby, K.; Milne, C. P., Jr.; Krell, P.; Wild, J. R. Transfer and expression of an organophosphate insecticide-degrading gene from *Pseudomonas* in *Drosophila melanogaster*. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 1–5.
(64) Rowland, S. S.; Speedie, M. K.; Progell, B. M. *Appl. Environ. Microbiol.* **1991**, *57*, 440–444.
(65) Dumas, D. P.; Caldwell, S. R.; Wild, J. R.; Raushel, F. M. *J. Biol. Chem.* **1989**, *264*, 19659–19665.
(66) Cheng, T.-c. Personal communication, 1991.
(67) Kopec-Smyth, K. Personal communication, 1991.
(68) Lunzer, J. A. Personal communication, 1991.
(69) Harvey, S. P.; Height, J. J.; Szafraniec, L. L.; Beaudry, W. T.; DeFrank, J. J.; Valdes, J. J.; Chakrabarty, A. M. Biodegradation of Mustard. In *Abstracts of 91st Annu. Meet. Am. Soc. Microbiol.* Dallas, TX, May 1991, Abstr. Q119.
(70) For a review, see: (a) Coon, M. J.; White, R. E.; Groves, J. T. In *Metal Ion Activation of Dioxygen*; Spiro, T., Ed.; John Wiley: New York, 1980; pp 73–162. (b) Drago, R. S. *Coord. Chem. Rev.* **1992**, *117*, 185–213.
(71) Drago, R. S. Personal communication, 1991.
(72) For a review, see: (a) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125–131. (b) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69.
(73) (a) Yang, Y.-C.; Buchannan, J. H.; Rohrbaugh, D. K.; Szafraniec, L. L.; Beaudry, W. T. *The Photocatalytic Oxidation of HD on Titania Surfaces*; CRDEC-SP-005, May 1989. (b) Buchanan, J. H.; Rohrbaugh, D. K.; Szafraniec, L. L.; Beaudry, W. T.; Yang, Y.-C. Photocatalytic Air Oxidation of HD and VX. In *1989 In-house Laboratory Independent Research (ILIR) Report*; CRDEC Special Report, in press. (c) Fox, M. A.; Kim, Y.-S.; Abdel-Wahab, A. A.; Dulay, M. *Catal. Lett.* **1990**, *5*, 369–376.
(74) For a review, see: Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314.
(75) Hovanec, J. W.; Albizo, J. M.; Henderson, V. D. Dissolution Studies of Thickened Agent and Simulants in Mixtures of Water, N-Alkyl Pyrrolidinones and Surfactants. In *Proceedings of the 1990 U.S. Army CRDEC Scientific Conference on Chemical Defense Research*; U.S. Army CRDEC: Aberdeen Proving Ground, MD, in press.
(76) Szafraniec, L. L.; Beaudry, W. T. 1991 Unpublished NMR results on the reactions of the new decontaminant, DAM (Decontaminating Agent: Multipurpose), with HD, VX, GB, and GD, 1991.
(77) Ember, L. R. Chemical Weapons Disposal: Daunting Challenges Still Ahead. *Chem. Eng. News* **1990**, *68*, 9–19.
(78) U.S. Congress, Office of Technology Assessment, *Disposal of Chemical Weapons: Alternative Technologies-Background Paper*, OTA-BP-O-95, June 1992; U.S. Government Printing Office: Washington, DC, 1992.

REVIEW OF INFORMATION/INFORMATION MATERIALS PAO-99-365

1. AUTHOR/COTR Extension Office Symbol
Harvey W Yurow, Ph.D.
George T. Davis, Ph.D.

2. MATERIAL CLASSIFICATION
(Circle one): (UNCL) CONF SECRET
Distribution Limited

3. TYPE OF MATERIAL
X Technical Report
__ Technical Note
__ Oral Presentation
__ Poster Session
__ Contractor Report
__ Special Publication
__ Abstract
__ Other

4. FUNDING CATEGORY. (Circle one)
6.1 6.2 6.3. 6.4
6.5 Customer (if customer, please identify) Other

5. TITLE: Chemical Systems Laboratory Technical Report ARCSL-TR-81080 Decontamination and Disposal Methods For Chemical Agents — A Literature Survey

6. TYPE OF RELEASE.

X UNLIMITED DISTRIBUTION. Statement A (Public Release)
__ LIMITED DISTRIBUTION. Select statement below (check one only) and give applicable reason (see chart on page 4 of this form)
__ B - U.S. Government agencies only
__ C - U.S. Government agencies and their contractors only
__ D - DoD and U.S. DoD contractors only
__ E - DoD Components only
__ F - Further dissemination only as directed by Cdr, Chemical and Biological Defense Command (CBDCOM) or his designee.
__ X - U.S. Government agencies and private individuals or enterprises eligible to obtain export-controlled technical data

REASON: Wash Chemical Agent Rule Repository

__ Classified Material

Security Classification Authority, CLASSIFIED BY:_____

Declassification or Downgrading Instructions, DECLASSIFY ON:_____
DOWNGRADE ON:_____

7. Attached will____will not____be presented to foreign nationals or presented at a symposium where foreign nationals or foreign representatives will be present. (If answer is "will" or "unknown", contact the Counterintelligence Office (Foreign Disclosure) for assistance.) (For Limited Distribution Only)

8. Name and address of periodical (if for journal publication):

_____

_____

_____Refereed _____Non refereed

9. Forum:_____

Title:_____

Location_____

Date_____

DoD sponsored: ___Yes ___No

10. Attached has____has not____been coordinated with contractor. Name and address of contractor:

_____

_____

_____

11. Invention/work described herein has___ has not____been forwarded to Office of the Chief Counsel CBDCOM.

Name of inventor_____

Organization_____

File Number of Invention_____

12. Portion of attached was __ was not__ extracted from copyrighted source.

Source Documentation: _____

Permission granted by _____

(Correspondence Attached)

AD

CHEMICAL SYSTEMS LABORATORY TECHNICAL REPORT

ARCSL-TR-81080

DECONTAMINATION AND DISPOSAL METHODS FOR CHEMICAL AGENTS – A LITERATURE SURVEY

by

Harvey W. Yurow, Ph.D.
George T. Davis, Ph.D.

Research Division

November 1982

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

DISCLAIMER NOTICE

This document may contain pages which do not reproduce legibly. Inconsistent page numbers are due to omittance of blank pages.

JCP-I, DPG

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-81080	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DECONTAMINATION AND DISPOSAL METHODS FOR CHEMICAL AGENTS – A LITERATURE SURVEY		5. TYPE OF REPORT & PERIOD COVERED Technical Report May-September 1980 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Harvey W. Yurow, Ph.D. George T. Davis, Ph.D.		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander, Chemical Systems Laboratory ATTN: DRDAR-CLB-R Aberdeen Proving Ground, Maryland 21010		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS C911.010707
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, US Army Toxic and Hazardous Materials Agency ATTN: DRXTH-ES Aberdeen Proving Ground, Maryland 21010		12. REPORT DATE November 1982 13. NUMBER OF PAGES 46
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to US Government agencies only because of test and evaluation; November 1982. Other requests for this document must be referred to Commander, US Army Toxic and Hazardous Materials Agency, ATTN: DRXTH-ES, Aberdeen Proving Ground, Maryland 21010.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Decontamination	GB
Explosive containment system	VX
ECS	HD

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A proposed explosive containment system (ECS) is to be used for demilitarization of unmarked chemical munitions in the field. Input is needed for destruction of each of the possible agents that may be encountered. Therefore, a literature survey has been made of decontamination methods for the more common agents. Based upon this survey, recommendations have been given for the best method of disposal for each agent.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PREFACE

The work described in this report was authorized and funded by Environmental Technology Division, Demil/Disposal Branch, under the title, "Explosive Containment System. Method for Agent Identification, Decontamination and Certification, C911.01.0507." The work was begun in May 1980 and completed in September 1980.

CONTENTS

DECONTAMINATION AND DISPOSAL METHODS FOR CHEMICAL AGENTS – A LITERATURE SURVEY

1. INTRODUCTION

A request was made for a review of liquid methods applicable to disposal of certain agents by US Army Toxic and Hazardous Materials Agency (USATHAMA). This information was to be utilized in the selection of systems for decontamination/disposal in an "explosive containment system" (ECS). As presented to us, the suspected agents are contained in ordnance with a charge of explosives. The concept is to detonate the ordnance with added explosives in an ECS without down loading the agent or burster charges. The concept is primarily intended for liquid-filled rounds including gases that are liquid under pressure. Some solid-filled rounds may also be amenable for disposal by this method. Liquid and solid fills will be differentiated by X-ray technique. Specifically excluded are high explosive (HE)-filled rounds. After the explosion in the ECS, the explosion "products" may be decontaminated by either a liquid reaction or by being fed into an incinerator, with the selected option depending on logistical and engineering parameters and trade-offs. This paper supplies technical information toward evaluating the chemical requirements of a liquid decontamination option.

In the liquid decontamination option, the contents of the ECS would be decontaminated with liquid reactants to neutralize the residual intact agent(s) present. The resulting decontaminated brines could be then placed into drums and transported to an existing demilitarization facility for final disposal.

No glycolates are involved. Suspected fills include GB, GD, VX, H, HD, L, GA, HN, CG, PS, AC, CK, and BBC.

After a discussion of the general problem area, it was proposed that a complete and detailed review be accomplished, which could prove a valuable reference in other decontamination/disposal operations.

The subject of decontamination can prove to be a challenging area because of the chemical breadth of the material, the variety of situations to which it is applied, and the detailed sophistication required to draw satisfactory conclusions for reduction of chemical data to actual field or engineering practice. For example, skin decontamination, field decontamination of equipment and materiel, and decontamination for disposal operations have uniquely different criteria for selection of a satisfactory system.

The choice of decontaminants for disposal operations can be based upon some of the following requirements:

(a) High reagent capacity.

(b) Well-defined products of known toxicity.

(c) Thermal moderation (ease of control).

(d) "Reasonable" rate.

(e) Low flammability for safety in handling.

(f) Economy.

(g) Special corrosion problems.

(h) Vapor or skin toxicity.

(i) Ease of incineration.

(j) Nature of incineration products.

Actual selection of a decontaminant cannot be made until a choice is made of the relative importance of the various criteria.

Other criteria may arise in special instances. The base-line data for selection, which have involved chemical studies, include information related to (a), (b), (c), (d), (g), (i), and (j). One will infrequently encounter all of the necessary information, but certain information is usually available for systems that have been studied, allowing a preliminary judgment to be made. The following appear to be minimally necessary:

(a) Determination of heat of reaction or ad hoc demonstration of thermal control of the reaction system to be utilized (see table A-1, appendix).

(b) Determination of kinetic rate constants or ad hoc demonstration of completeness of reaction within a suitable time frame (see table A-2, appendix).

(c) Demonstration of reaction products and stoichiometry or sufficient assessment to eliminate criticality of procedure when the system is applied (see tables A-2 and A-3, appendix).

(d) Ability to calculate gravimetric factors for active ingredients at least as a worst-case assessment (see table A-2).

(e) Ability to calculate, reliably, a minimal capacity factor in volume of decontaminant per gram of agent or weight of decontaminant per gram of agent (see table A-2).

(f) Analytical procedure for residual agent.

Therefore, in respect to the special problems confronting disposal, we have attempted to assemble these critical elements for disposal systems insofar as is possible. We are providing fundamental chemistry, as well as chemistry of those systems that have been inadequately explored, to ensure that sufficiently sophisticated viewpoints become available to rationalize decontaminant choice or to be able to explore promising alternatives not yet in use. Also, we hope that the deficiencies of some of the systems can become evident by a brief description of available, but incomplete, information. The following list[1,2] provides chemical nomenclature and symbols for the agents under consideration:

(GA, Tabun) ethyl dimethylphosphoramidocyanidate

(GB, Sarin) isopropyl methylphosphonofluoridate

(GD, Soman) pinacolyl methylphosphonofluoridate

(VX) O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate

(H, HD, mustard) 2,2'-dichloroethyl sulfide 2,2 chloro ethylsulfide

(HN-1, nitrogen mustard) bis(2-chloroethyl)ethylamine

(HN-2) bis(2-chloroethyl)methylamine

(HN-3) tris(2-chloroethyl)amine

(L, lewisite) 2-chlorovinyldichloroarsine

(CG) phosgene

(AC) hydrocyanic acid

(CK) cyanogen chloride

(PS) chloropicrin

(BBC, CA) 2-bromobenzyl cyanide

The decontamination of each of these agents will be discussed, in turn, with specific reference to:

(a) Physical properties that are of importance in decontamination; i.e., water solubility and boiling point.

(b) Criteria for selection related to:

(1) Reaction equations.

(2) Kinetics.

(3) Heat evolution.

(4) Effectiveness.

(c) *Analytical methods for determination of residual agent in decontamination solutions* with respect to:

(1) Sensitivity level.

(2) Reliability.

(3) Ease of application.

In addition, a discussion will be given on whether there is a "best choice" decontaminant recommended for unknown fills or whether incineration might be the only option. Tables A-1, A-2, and A-3 also provide comparisons and summaries of some of the developed information.

2. THE DECONTAMINATION OF VARIOUS AGENTS

2.1 Ethyl dimethylphosphoramidocyanidate (GA).

2.1.1 Selected physical properties. Ethyl dimethylphosphoramidocyanidate, which is miscible with water, has a boiling point of 237°C.[3]

2.1.2 Decontamination. Destruction of the agent is most easily accomplished by hydrolysis in aqueous sodium hydroxide.

$$(H_3C)_2N-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O}{\|}}{P}}-CN + 2NaOH \longrightarrow (H_3C)_2N-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O}{\|}}{P}}-ONa + NaCN + H_2O$$

The pseudo-first-order rate constant for hydrolysis of GA has been reported as being 0.02 min^{-1} at pH 9.5 and 25°C;[4] whereas, the heat of reaction was given as -10.1 kcal/mole.[5] The hydrolysis of GA in seawater has also been studied.[6*] The hydrolysis in water proceeds by two independent paths, depending upon the pH of the water.[7] At lower values, dimethylamine is produced; whereas, at higher pH, cyanide ion is liberated. In seawater, the latter route is favored. The following data were obtained at various temperatures.

Table 1. Half Life of GA in Seawater at Three Temperatures

Temperature	$t_{½}$
°C	min
15	475
20	267
25	175

The destruction of toxic cyanide ion from hydrolyzed GA is readily accomplished by oxidation with hypochlorite in basic solution, as described below in the section on hydrocyanic acid.

* Epstein, J., Rosenblatt, D. H., Gallacio, A., and McTeague, W. F. Draft Report to Commanding General, US Army Munitions Command, ATTN: AMSMU-MS-CH, Dover, New Jersey, Subject: Chemical Disposal Operations. Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations. 2 October 1972. UNCLASSIFIED Report.

2.1.3 Analysis.

Methods for the analysis of trace amounts of agents in decontamination solutions usually involve a preliminary extraction of the agent into an organic solvent such as chloroform or hexane. This is necessary because the large excess of salts present will often interfere in the analytical method used. No study has been reported on the recovery of trace amounts of GA from aqueous sodium hydroxide, but it is likely that the compound can be extracted by chloroform, as has been reported for the water miscible GB.[8,9] Once the GA has been extracted, there are a number of methods available for its assay. Two sensitive colorimetric procedures for the determination of organophosphates, such as GA, are the Schönemann reaction with o-dianisidine and peroxide[10] and the diisonitrosoacetone reaction[11] with sensitivities of the order of 0.2 μg/ml in the final solutions. A fluorimetric technique using indole,[12] with sensitivity comparable to that of the colorimetric techniques, has been reported. Even more sensitive are enzymatic methods[13] involving acetylcholinesterase and colorimetric, fluorimetric,[14] or electrometric measurements, but these are subject to a considerable number of interferences.[15]

Many of the interferences in the above procedures can be removed prior to analysis of the agent by gas-liquid chromatographic (GLC) or thin-layer chromatographic (TLC) methods. The GLC procedure is the one customarily used for the assay of agents in organic extracts of decontamination solutions. A variety of columns is available for this purpose.

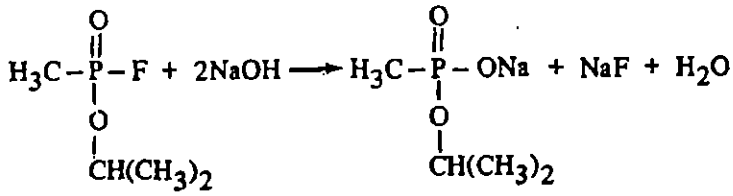
Separation prior to analysis is also possible with TLC techniques. The R_f values and semi-quantitative measurements have been made for a number of G agents using the well-known perborate-dianisidine or cholinesterase-indoxyl acetate sprays. As an alternative, the spot has been scraped off the plate and analyzed in a test tube, using standard colorimetric or fluorimetric methods.

2.2 Isopropyl methylphosphonofluoridate (GB).

2.2.1 Selected physical properties. Isopropyl methylphosphonofluoridate is completely miscible with water and boils at 151°C.[13]

2.2.2 Determination.

The most widely used method for the destruction of GB involves treatment with aqueous sodium hydroxide; i.e.,[16,17*]



The second-order reaction rate is 30 m^{-1} sec^{-1} and the heat of reaction is -44.4 kcal/mole.[16] With 5% aqueous sodium hydroxide, the half life is <0.8 sec. If the reaction mixture contains aluminum

* Kokalas, J. J., Sommer, H. Z., and Porter, G. Quarterly Progress Report. Research Plan No. 3397. Operation Red Hat. Defense Research Branch. 16 March 1973. UNCLASSIFIED Report.

metal (such as from a munition), then 10% aqueous sodium carbonate is recommended, to avoid hydrogen evolution, with a first-order rate constant of 0.08 sec^{-1}, a $t_{1/2}$ of 8.45 seconds, and a destruction efficiency of >99.9999%. The heat of the reaction (ΔH) for the carbonate process (10% sodium carbonate) has been estimated to be -22 kcal/mole.[8] This was shown to give a "safe" temperature rise of 2.58°C for an adiabatic process using 300% excess reagent (1 pound of GB per 7 gallons of 10% sodium carbonate).

$$GB + 2Na_2CO_3 + H_2O \longrightarrow CH_3-\overset{\overset{O}{\|}}{\underset{\underset{OC_3H_7}{|}}{P}}-ONa + NaF + 2NaHCO_3$$

Thermal tests have been conducted directly on M55 rocket warheads for the reaction of GB with sodium carbonate.* In these tests, the decontaminant was constantly flushed and agitated during the operation. Acceptable temperature rises were obtained even in the intimate presence of reacting explosives and reagents. The temperature rise was monitored by thermocouples at several locations. From an initial 74°F to 99°F, the highest temperature rise, 21°F (12°C), was at or near the decontaminant inflow. These tests were conducted under evaluation of the Johnston Island plan for disposal operations (table A-1).

Several other reviews exist which include further chemistry of GB.[18-22] The reactions are, in general, not sufficiently studied to develop full criteria for their usefulness in disposal processes. The most notable reagent that has received attention is the hypochlorite ion (present in various forms of bleach). It possesses a second-order rate coefficient for reaction with GB that is very large (10 M^{-1} sec^{-1} at 25°C). Although "catalytic" in action, much of the advantage of "catalysis" is lost by the need to use large amounts of buffer or neutralizing bases if a large capacity is to be achieved. For the hydrolytic hypochlorite reaction with GB,[18] the phosphonic acid anion and fluoride anion are produced as indicated in the previous equation. Reactions of GB with DS-2** and CD-1† (or ADP) are vigorous and rapid.[22]

The problem related to salt disposals from GB neutralization reactions with various strong bases is now well known.[23-25] The spray-drying operation results in the trace "regeneration" of GB and the need for special procedures to prevent emission of GB into the atmosphere. For this reaction, it might be desirable to produce a nonaqueous combustible product from the neutralization stage which would allow direct combustion without spray drying. This approach has not been tested. Early in the program for disposal of the war gas identification sets, the decision was made to avoid inorganic salts because of increased disposal problems caused by their presence. Consequently, monoethanolamine was widely employed as a decontaminant. However, this reagent has not been evaluated against GB, nor has the combustion of the products been studied, to assess the possibility of emission of GB reformed during that combustion process. The reaction has been investigated,[6,8] however, in connection with use of monoethanolamine as a scrubber substance.

* Kokalas, J. J., Sommer, H. Z., and Porter, G. Quarterly Progress Report. Research Plan No. 3397. Operation Red Hat. Defense Research Branch. 16 March 1973. UNCLASSIFIED Report.

** DS-2 is 2% sodium hydroxide, 28% 2-methoxyethanol, and 70% diethylenetriamine, all by weight.

† CD-1 is 2.5% lithium hydroxide hydrate, 55% 2-aminoethanol, and 45% 2-hydroxy-1-propylamine, the latter two by volume.

Decomposition rates for GB in soil and in seawater[6,26] have also been reported. The half life in seawater is about 8 hours at 25°C; whereas, for reservoir water,[27] the values at 25°C are 237 hours at pH 6.5, 75 hours at pH 7.0, 24 hours at pH 7.5, and 7.5 hours at pH 8.0. For soil, the values are 2.5 to 25 hours at 15°C depending upon moisture content.[6] Wet soil could possibly afford a moderated, useful, slow decontaminant for GB.

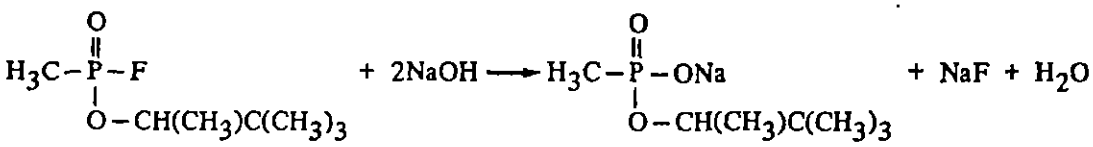
2.2.3 Analysis. Various reports have appeared on the analysis of GB residues in aqueous sodium hydroxide or sodium carbonate.[8,9,25,28,29] As mentioned under the analysis of GA, extraction of the brines with an organic solvent, such as chloroform, was followed by a wet chemical method of analysis[10-15] or by a GLC procedure.[8,9,25,28,29*]

2.3 Pinacolyl methylphosphonofluoridate (GD).

2.3.1 Selected physical properties. Pinacolyl methylphosphonofluoridate is appreciably less soluble in water than is GB and the boiling point is 167°C.[3]

2.3.2 Decontamination.

As with the other G agents, reaction with sodium hydroxide is considered to be the best method for use with munition fills. However, the lower aqueous solubility of GD as compared to GA and GB necessitates the use of a mixed aqueous-organic solvent if the decontamination is not to be unduly prolonged in a heterogeneous system. Because of its higher flash point, 2-methoxyethanol[30] is recommended for this purpose over methanol or ethanol and has been reported for decontamination in a mixture containing 70 parts (w/w) of the organic solvent with 30 parts (w/w) of 50% aqueous sodium hydroxide.



The reaction rate is comparable to that for GB, with a reported complete destruction within 5 minutes in excess 5% aqueous sodium hydroxide.[3] The heat of reaction should be comparable to that given for GB (–44.4 kcal/mole), as the same leaving group is involved (table A-1).

2.3.3 Analysis. Procedures for GD are similar to those described for the other organophosphates; e.g., extraction from the brine, followed by gas liquid chromatography or a colorimetric or fluorimetric analytical method.[8-15,26,28,29]

2.4 O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (VX).

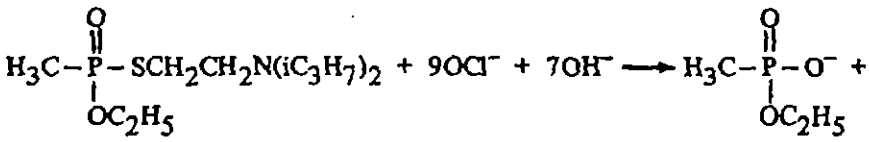
2.4.1 Selected physical properties. The solubility of O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate in water is 3 gm/100 gm at 25°C and the boiling point of VX is 298°C.[13]

* Kokalas, J. J. Quarterly Progress Report. Research Plan No. 3397. Operation Red Hat. Defense Research Branch. 22 June 1973.

2.4.2 Decontamination.

Three decontamination systems have been used for bulk amounts of VX; aqueous calcium hypochlorite (HTH) slurry, acid chlorinolysis, and aqueous sodium hydroxide. Each system has its advantages and disadvantages.

The hypochlorite slurry method has the following stoichiometry:*



$$H_3C-P(=O)(OC_2H_5)-SCH_2CH_2N(iC_3H_7)_2 + 9OCl^- + 7OH^- \longrightarrow H_3C-P(=O)(OC_2H_5)-O^- +$$

$$HN(iC_3H_7)_2 + SO_4^{=} + 2CO_3^{=} + 9Cl^- + 5H_2O$$

It should be noted that the stoichiometry written for this reaction is an assumed one, which is based on partial and fragmentary evidence. The estimate for the heat of reaction also appears to have many uncertainties.** However, the calculated heat of reaction (from bond energies, etc.) of 685 kcal/mole agreed closely with an experimental value of 675 ± 13 kcal/mole.† This may be a fortuitous result. In view of some of the product complexities observed in a similar type of reaction with H (sulfur mustard, to be described later), this decontamination can only be recommended cautiously should a high degree of certainty in products and thermochemistry be required. The quoted first-order rate constant is not well defined. It is known that the reaction occurs in stepwise fashion, and the sequential stoichiometry is not known. Clearly, additional work should be performed before utilization of this reaction in a disposal process.

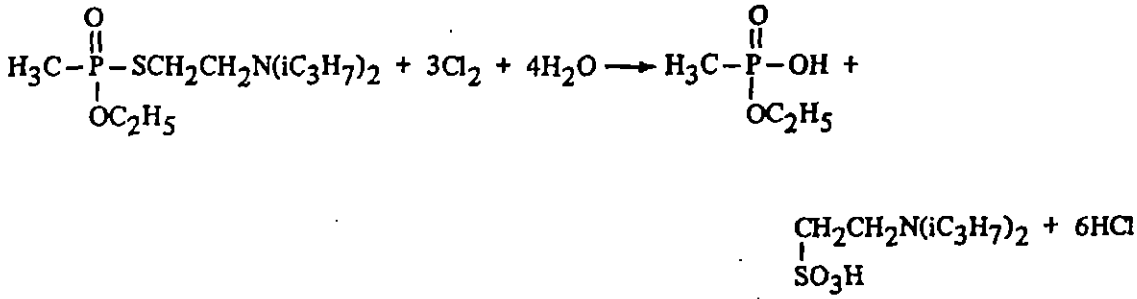
The experimentally determined first-order rate constant is approximately 0.01 sec^{-1}. Using the value for the heat of reaction of approximately 700 kcal/mole, the heat rise equation is $T\ (°C) = \frac{\text{moles of VX (275)}}{\text{gallons of 10\% HTH}}$ (Epstein, J., 23 May 1973; see footnote). Although the reaction is theoretically a rapid one, in actuality it occurs more slowly than predicted because of the heterogeneous nature of the system. It was considered for the demilitarization of VX in a disposal project at Tooele Army Depot,[28] but it was found to be less effective than was acid chlorinolysis because of the possibility of incomplete reaction if the pH value falls below 11. To avoid this, a large excess of hypochlorite was required. Destruction of VX was then found to be better than 99.9999%.

* Epstein, J., Edgewood Arsenal. Disposition Form to Chief, Demil/Disposal Office. Heat of Reaction of VX with Alkaline Bleach Solution. 23 May 1973. UNCLASSIFIED Disposition Form.

** Pistritto, J. V. Private communication. Mr. Pistritto estimated that the calorimetric system utilized has inaccuracies of the order of 10%, even under optimal conditions, due to heat losses to the surroundings.

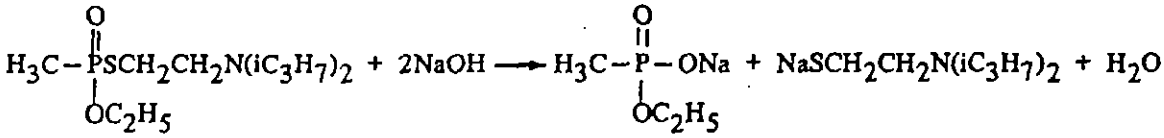
† Kokalas, J. J. Quarterly Progress Report. Research Plan No. 3397. Operation Red Hat. Defense Research Branch. 22 June 1973. UNCLASSIFIED Report.

A second system involves acid chlorinolysis of VX; i.e.,[31]



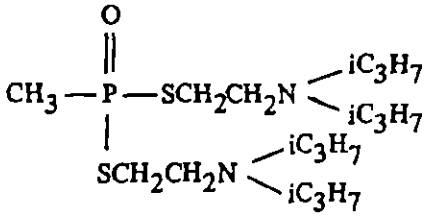
As neat VX may burn on contact with chlorine gas, the VX was first dissolved in 1.5 N hydrochloric acid. The chlorination was highly exothermic and rapid [half life ($t_{1/2}$) is 1.2 minutes at pH 4],[32] it required cooling, and it was found to be 99.999999% efficient. A major limitation of the method is the high corrosiveness of the mixture to metals, such as those that are present in the ECS.

The third decontaminant for VX is sodium hydroxide, either in an aqueous or in an organic-aqueous medium; i.e.,

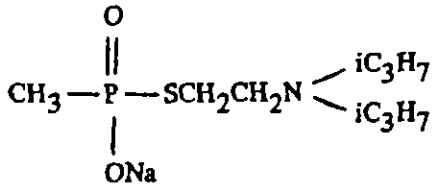


The half life of VX at pH 14 is 1.3 minutes; but, because of its low solubility in water, the reaction requires a considerably longer time unless an organic solvent such as 2-methoxyethanol is included. Using 10% aqueous hydroxide, Monsanto[33] reported the destruction of bulk amounts of VX in 6 to 8 hours at ambient temperature, with air stirring.

Similar studies were reported by the Navy.[34] A total of 12-½ gallons of VX was decontaminated using 150 gallons of 10% aqueous sodium hydroxide (air agitated) in three stages (50-gallon addition, each stage). The solubility of VX was incomplete, initially. The last two stages employed heated sodium hydroxide solutions. The time for the "complete" decontamination was 6 to 8 hours. The solubilization problem indicates that this method of decontamination will be unreliable unless the mixing process is very adequately controlled. It must also be noted that, if the reacting VX contains the "bis impurity"[35] (I), the action of base will generate the refractory substance (II), which will not undergo further hydrolysis.[35] This substance is highly toxic and by itself would not pass Department of Transportation standards for transport to a disposal site; however, the amount of bis in VX would normally be less than 10%.



I



II

In addition, results reported by Southern Research Institute[22] indicate that similar caution must be applied to the toxicity of products from VX-hypochlorite reactions. In these studies, it was shown that DS-2 or CD-1 decontamination of VX yielded products with toxicities that were much lower than those achieved by the hypochlorite method. Even after 30 to 60 minutes of decontamination time, the latter mixtures remained highly toxic.

Ad hoc thermochemical (thermal profiles)* studies have been conducted for M55 warheads and M23 land mines containing VX which were allowed to react with circulated mixtures of 100 pounds of HTH in 120 gallons of water. These tests demonstrated adequate control of the temperature rise of this reaction under the specific set of conditions utilized.

The subjects of hydrolysis of VX in seawater and decomposition of VX in soil have also been reviewed.[6] In the former case, the hydrolysis of the "bis analog" (I) would give rise to the toxic refractory product (II) aforementioned. Hydrolysis in seawater would require up to 400 years to reduce VX toxicity to 1/1000 of its initial value. In soil, VX would undergo approximately 95% decomposition in 10 days with temperature, organic matter content, and perhaps moisture content being contributing factors.

Under current investigation** is the detoxification of VX using sodium dichloroisocyanurate ("Fichlor") for disposal purposes. The reaction is preferably carried out at pH 6 or lower. Products are variable, and definite kinetics cannot be established because of the sequential nature of the reactions. A precipitate of isocyanuric acid is produced as a result of reaction. Detergents are found to be ineffective in promoting solubilization of VX in the solution in order to speed up its destruction. The reaction bears similarities to the reaction of aqueous bleach with VX, but the reagent is less corrosive than bleach.

Of the three aforementioned methods, one would tentatively recommend the calcium hypochlorite slurry procedure for the ECS provided that a suitable analytical method were developed (see below). The acid chlorinolysis is too corrosive and the sodium hydroxide reaction is nonhomogeneous and relatively slow. Lack of a sufficient data base precludes consideration of sodium dichloroisocyanurate.

2.4.3 Analysis.

A variety of sensitive methods has been developed for the estimation of trace amounts of VX. However, a considerable number of problems have been encountered in their application to decontamination solutions because of the presence of numerous byproducts.† In the procedure involving acid chlorinolysis,[31] the solution was made basic to pH 10 and was extracted with dichloromethane. The VX in the extract was determined fluorimetrically using indole (sensitivity, 30 μg/l of brine), enzymatically, after TLC

* Kokalas, J. J. Quarterly Progress Report. Research Plan No. 3397. Operation Red Hat. Defense Research Branch. 22 June 1973.

** Hovanec, J. W., Davis, G. T., and Epstein, J. Chemical Systems Laboratory. Unpublished results. 1978.

† Wagner, P., Edgewood Arsenal. Demil Progress Report, Omnibus Program. 21 October 1976. UNCLASSIFIED Report. Wagner, P., Edgewood Arsenal. Demil Progress Report, Omnibus Program. 4 February 1977. UNCLASSIFIED Report.

separation (0.5 μg/l) and by a GLC procedure (40 μg/l) with a detection limit of 4 ng. Recent laboratory experiments involving gas liquid chromatography of VX extracts from chlorinolysis brines indicated a considerable number of interferences and greatly reduced sensitivity.*

In the analysis of VX from HTH brines, problems have arisen involving poor extraction recoveries, which have not been resolved, and sensitivities have been low (600 μg/l of brine).** Yet, detailed procedures have been described for such analyses from dilute HTH solutions.[36]

2.5 2,2'-Dichloroethyl sulfide (HD).

2.5.1 Selected physical properties. The solubility of 2,2'-dichloroethyl sulfide in water is 0.1 gm/100 gm and the boiling point is 215° to 217°C.[1]

2.5.2 Decontamination.

The two most widely used decontaminants for HD are 2-aminoethanol (monoethanolamine, MEA)[37,38] and aqueous calcium hypochlorite slurry.[1] The use of MEA has a number of decided advantages† including: relatively high flash point, relatively noncorrosive to metal, inexpensive, relatively stable, homogeneous reaction with HD, moderate heat of reaction, and volume ratio of only 5:1 required. The compound is somewhat toxic (threshold limit value is 3 ppm).[39] The reaction of HD and MEA is given by the equation:

$$\underset{\text{I}}{(ClCH_2CH_2)_2S} + 2HOCH_2CH_2NH_2 \longrightarrow \underset{\text{II}}{HOCH_2CH_2-\overset{Cl^-}{\overset{+}{N}}\!\!\begin{array}{l}\diagup\\ \diagdown\end{array}\!\!\begin{array}{l}\diagdown\\ \diagup\end{array}\!\!S} + HOCH_2CH_2\overset{+}{N}H_3\ Cl^-$$

The type of reaction represented by the above equation had received attention in the open literature,[40] but quantitative studies of products' kinetics and thermochemistry were not reported. A decided advantage of these systems is the absence of inorganic salts in the final disposition process.

The half life of the reaction was reported as being 11 minutes at 57°C and 40 minutes at 44°C. The heat of reaction at 50°C was -40 kcal/mole, which was the initial temperature at which the decontamination was usually carried out. Above this temperature, the heat of reaction increased significantly and cooling was required with a 5:1 v/v ratio of MEA to HD; the adiabatic temperature

* Yurow, H. W., and Valis, R. CSL unpublished results. 1979.

** Wagner, P., Edgewood Arsenal. Demil Progress Report, Omnibus Program. 21 October 1976. UNCLASSIFIED Report. Wagner, P., Edgewood Arsenal. Demil Progress Report, Omnibus Program. 4 February 1977. UNCLASSIFIED Report.

† Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Toxic War Gas Sets. 28 March 1974. UNCLASSIFIED Disposition Form.

rises were from 50°C (initial) to 113°C (final) and 65°C (initial) to 151°C (final).* With the MEA method, residual amounts of HD from batches of 60 gallons of HD and 300 gallons of MEA were <0.25 mg of HD/l.[36]

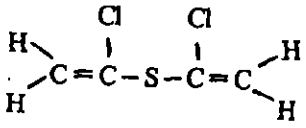
Studies have indicated that, for MEA with chloroform present (as in kit solutions and in certain munitions fills, e.g., chloropicrin), a delayed, violently exothermic reaction sometimes occurred in closed vessels,** which required that the mixture be heated in an inert atmosphere at 100°C to destroy the chloroform prior to storage. But as chloroform does not accompany HD in munitions, this treatment would not be necessary.

The above-cited hazard of a slowly appearing exotherm, which nevertheless results in a violent runaway reaction upon storage, is not an isolated instance in the history of stored materials resulting from disposal operations. Detailed methods and apparatus are now being developed for safely eliminating the appearance of such unpleasant surprises.[41] Analyses of various systems are performed by computer-controlled adiabatic calorimetry with computer data processing. Other approaches to the problem have been the previous use of DTA (differential thermal analysis) and DSC (differential scanning calorimetry), but the approach cited in the above reference develops much more complete information for analysis, if an actual problem exists. Detection of the problem should be adequately performed, however, by DTA or DSC or both. It is recommended in the present operations that such studies be run on all stored detoxified materials prior to substantial use of the method or to transportation of the resulting mixture of chemicals. Hidden exotherms in the gummy mixture from the explosive containment operation and the subsequent decontamination operation would not escape recognition.

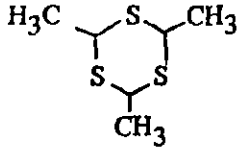
Aqueous reactions of H or HD are generally to be avoided because of the solution problems and the heterogeneous nature of the reactions. This results in uncertainty as to completeness of reactions and greater difficulties in controlling or moderating the reactions. Although bulk quantities of HD can be decontaminated with aqueous bleach (such as HTH slurry), and an assumed stoichiometry (worst case) may be utilized for the reaction, the actual products may contain many poorly identified materials whose toxicities have not been assessed.[42] For example, among the products detected from halogen reactions (usually in carbon tetrachloride) with sulfur mustard are the following:

$$ClCH=CH-S-CH_2CH_2Cl$$

III



IV



V

$$ClCH_2CH_2S-CCl=CHCl$$

VI

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Toxic War Gas Sets. 28 March 1974. UNCLASSIFIED Disposition Form.

** Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Toxic War Gas Sets. 18 December 1974. UNCLASSIFIED Disposition Form.

Cold halogenation of mustard has been shown[43] to produce an unstable adduct VII which decomposes to give a mixture of products containing VIII and IX.

$$(ClCH_2CH_2)_2-S^{\oplus}\ X\ X^{\ominus}$$

VII

$$CH_2=CCl-S-CH_2CH_2Cl \qquad + \qquad ClCH=CH-S-CH_2CH_2Cl$$

VIII IX

Other reported compounds include the sulfoxide X:[44]

$$ClCH_2CH_2-\underset{\underset{O}{\|}}{S}-CHCl-CH_2Cl$$

X

Because no complete material balance on the reaction of HD mustard with various bleaches has been achieved, the absence of the above products cannot be assumed, even in aqueous solutions.

So-called "kinetics" of the reaction of bleach with mustard cannot be analytically interpreted or applied predictively on any basis other than an ad hoc situation identical to that reported. The reasons are that the stoichiometry is indefinite, and the sequential stoichiometries are unknowns. Thus, it is impossible to choose a mathematical model for the reaction. A worst-case stoichiometry can be assumed for calculation of the ultimate capacity of bleach systems. That stoichiometry is as follows:

$$(CH_2CH_2Cl)_2S + 7Ca(OCl)_2 + 2Ca(OH)_2 \longrightarrow CaSO_4 + 8CaCl_2 + 4CO_2 + 6H_2O$$

The use of aqueous sodium hydroxide solutions for decontamination of HD has been espoused;[20] but, kinetically, there is little basis for effectiveness at or near ambient temperatures. Furthermore, if hydrolyzed in water,[45] derivatives of vinyl sulfides are produced, as well as are syrupy residues containing various adducts and condensates (some of which are sulfonium derivatives) of mustard and "semi"-mustard (hydroxyethylchloroethyl sulfide), leading to a residue that can only be poorly characterized.

2.5.3 Analysis.

A technique has been reported* for the assay of HD in 2-aminoethanol. The solution was mixed with 10% aqueous sodium chloride to facilitate extraction and was extracted with hexane, which was then injected directly into a GLC system.[46] Amounts of HD down to 2.5 ppm in the analytical solution were readily determined. A similar procedure was used for the analysis of HD in

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Detection of Agents in Decontaminated Toxic War Gas Solutions. Undated. UNCLASSIFIED Disposition Form.

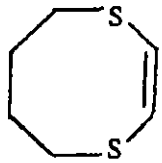
Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Simplified Methods of Analysis for H, HD, and HN-1 in Decontaminated Toxic War Gas Reaction Product Solutions. 20 March 1975. UNCLASSIFIED Disposition Form.

bleach solutions with a sensitivity of 1 ppm HD in hexane.* Further detailed procedures have been described for analysis of dilute HTH brines containing HD.[36]

An interesting artifact substance occurring in mustard samples was found during a study of pressurizing gases for DS-2 dispersers.** This substance was not readily separated from HD by GLC and interfered with achievable sensitivity limits for analysis of the HD. Mass spectral evidence was consistent with one of the following materials:

$CH_2=CH-S-(CH_2)_2-S-CH=CH_2$ XI

$CH_3CH_2-S-CH=CH-S-CH=CH_2$ XII



XIII

This substance will therefore probably not survive the attack of oxidizing decontaminants and it poses potential interference only in the case of alkaline (base) decontaminants such as DS-2 and CD-1.

The DB-3 technique [4-(4'-nitrobenzyl)pyridine][47] has also proven to be valuable for the estimation of mustard in the hexane extract either by silica gel-impregnated glass fiber sheets or by the M18 detector kit blue-band tube. Sensitivities of HD in the MEA solution were 2.5 ppm for each of the methods.

2.6 Nitrogen mustards: bis(2-chloroethyl)ethylamine (HN-1), bis(2-chloroethyl)methylamine (HN-2), and tris(2-chloroethyl)amine (HN-3).

2.6.1 Selected physical properties. The compound HN-1 has a solubility of approximately 0.5 gm/100 gm of water at ambient temperature,[6] it has a boiling point of 85°C at 10 mm, and it decomposes on boiling at atmospheric pressure. The agent HN-2 has comparable solubility to HN-1, with a boiling point of 75°C at 10 mm. The compound HN-3 is appreciably less soluble than the other two nitrogen mustards and it boils at 138°C at 10 mm.[3]

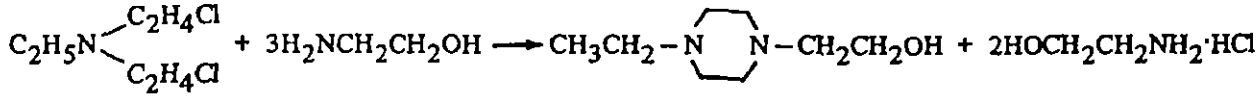
2.6.2 Decontamination.

The nitrogen mustards hydrolyze in water to give toxic products,[48] so that basic solutions are preferable for decontamination. The hydrolysis half life of HN-1 in dilute sodium hydroxide was

* Wagner, P., Edgewood Arsenal. Disposition Form. Analysis of HD in Aqueous HTH Solutions (Omnibus Program). 21 July 1973. UNCLASSIFIED Disposition Form.

** Daasch, L. W. Quarterly Progress Report. Research Plan 3350. Toxic Agent Destruction and/or Removal. Defense Research Branch, Chemical Laboratory, Edgewood Arsenal (APG). 17 September 1976. UNCLASSIFIED Report.

described as being 12 minutes at 18°C; but, because of the limited solubilities of the nitrogen mustards in this medium, a 2-aminoethanol decontaminant was preferred, with the reaction for HN-1 (and presumably for HN-2) being given as:*



The general reaction typified by the aforementioned process (amines with nitrogen mustards) has been reported in the open literature.[49,50] Kinetics have not been studied previously.

Kinetics for reaction of monoethanolamine (10 volumes of MEA in 1 volume of chloroform solution) were obtained** at 25°, 35°, and 45° with chloroform solutions containing 10% (volume) HN-1. The yield of N-ethyl-N'-hydroxyethylpiperazine (based on HN-1) was 99% ±10%.

Table 2. Reaction of HN-1 with Monoethanolamine (1 Volume of 10% HN-1 in Chloroform to 10 Volumes of Monoethanolamine)

Temperature	ko	$t_{½}$
°C	min^{-1}	min
25.1	0.020	34.6
34.9	0.060	11.5
44.9	0.137	5.1

The thermochemistry of this reaction has not been studied, but one might suspect similarities to the reaction of MEA and HD (table A-1, appendix).

There has been no study of aqueous oxidative methods of decontamination of the nitrogen mustards, except for some exploratory work.† A stirred chloroform solution of HN-1 in the presence of aqueous chlorine dioxide oxidant was shown to give a slow heterogeneous reaction. About 85% of the chlorine dioxide was transferred into the chloroform phase. The reaction was not further characterized.

* Defense Research Branch, Edgewood Arsenal. Disposition Form. The Decontamination of HN-1 in Chloroform in War Gas Identification Sets. 1974. UNCLASSIFIED Disposition Form.

Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Use of MEA as Decontaminant for Agents in Kits. 25 November 1974. UNCLASSIFIED Disposition Form.

** Pistritto, J. V., Davis, G. T., and Epstein, J. Quarterly Progress Report. Research Plan 3393. Decontamination of Agents in War Gas Identification Sets. Defense Research Branch, Chemical Laboratory, Edgewood Arsenal (APG). 10 June 1974. UNCLASSIFIED Report.

† Sarver, E. W. Quarterly Progress Report. Research Plan 3394. Defense Research Division. Decontamination of Agents in the War Gas Identification Set, Detonation, AN-M1A1, FSN 1365-323-7782. 22 June 1972. UNCLASSIFIED Report.

The reaction of nitrogen mustards in water proceeds in two steps through a substituted cyclic aziridinium* ion.[51] The first step to form the aziridinium ion is reasonably fast, but this ion is toxic[52] and relatively stable and it may be present for days or weeks in aqueous solution, depending upon the nature and concentration of nucleophiles present in solution.[51]

Values have also been obtained for the seawater solvolysis** and disappearance of HN-1. In seawater, the rate of approach to the equilibrium concentration of aziridinium ion underwent apparent increase, but the equilibrium concentration of aziridinium ion was depressed. The apparent half life of HN-1 at 4.5°C was about 25 minutes. At 25°C and pH 7.88, the half life was about 1.5 minutes in seawater. A half time of hydrolysis of all toxic materials from HN-1 was calculated to be about 12.5 days at 5°C in seawater.[6]

No study seems to have been made with HN-3 and 2-aminoethanol; but, as its general chemistry is similar to that of other nitrogen mustards, it is assumed that HN-3 can be deactivated by the reagent.

2.6.3 Analysis.

As with sulfur mustards, nitrogen mustards were determined by the DB-3 reaction. With the use of DB-3 impregnated-glass filter paper tickets,† the hexane extract of the MEA solution gave a positive test at 2.7 ppm of HN-1 in the decontamination mixture. This reagent was also employed to detect HN-1, HN-2, and HN-3 at 100 μg on TLC plates coated with silica gel.

A gas chromatographic procedure[46] (Crumb, E. A., 20 March 1975; see footnote) was developed for the assay of HN-1 in 2-aminoethanol solutions, which involved initial addition of 10% aqueous sodium chloride and extraction with hexane. Amounts of agent down to 3 ppm in 2-aminoethanol were measured.

2.7 2-Chlorovinyldichloroarsine (lewisite, L).

2.7.1 Selected physical properties. Lewisite is relatively insoluble in water, 0.05 gm/100 gm, and it has a boiling point of 190°C (reference 1, page 290).

2.7.2 Decontamination.

Although lewisite is only slightly water soluble, it reacts rapidly and is hydrolyzed to the relatively toxic and insoluble 2-chlorovinyl arsine oxide (reference 1, page 291). More effective is aqueous sodium hydroxide, which gives the less objectionable, but still toxic, sodium arsenite. Previous disposal of arsenical products from munitions involved burial at sea.[53]

* This ion is sometimes called the "ethyleneimmonium ion."

** Davis, G. T., Demek, M. M., Sarver, E. W., and Michel, H. O. Quarterly Progress Report. Research Plan 3391. Defense Research Division. Behavior of Chemical Agents Under Conditions of Chemical Disposal Operations. 22 June 1972. UNCLASSIFIED Report.

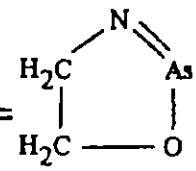
† Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Simplified Methods of Analysis for H, HD, and HN-1 in Decontaminated Toxic War Gas Reaction Product Solutions. 20 March 1975. UNCLASSIFIED Disposition Form.

Some reasonably comprehensive unpublished reviews of the literature on lewisite were accomplished in connection with "Decontamination of Agents in War Gas Identification Sets"* and chemical disposal.[6]** As mentioned above, hydrolysis in water is rapid to produce a gummy residue of lewisite oxide, which is in various stages of polymerization (depending upon age). Rates or mechanisms have not been studied. The thermochemistry has not been studied. The reaction with bleach is poorly characterized (Sarver, Research Plan 3394; see footnote). Stored lewisite contains three substances: lewisite I (L-1, 2-chlorovinyldichloroarsine), lewisite II (L-II, bis-2-chlorovinylchloroarsine), and arsenic trichloride. Hydrolysis in seawater is instantaneous (reference 6). Vesicant action is retained in soil for long periods of time (lewisite oxide). Oxidation of the lewisite oxide to the pentavalent state markedly reduces the toxicity. Because of the general toxicity of arsenic compounds (even in the pentavalent state), ultimate disposal presents some problems.

Reaction of lewisite with monoethanolamine has received some detailed study.† The reaction consists of a very fast process followed by a much slower reaction. The fast process has been characterized kinetically, thermochemically, and (partially) stoichiometrically.†† The slow process involves production of acetylene. The reactions are believed to be as follows:

$$ClCH=CH-AsCl_2 + H_2NCH_2CH_2OH \xrightarrow{k_1} ClCH=CH-As=NCH_2CH_2OH + 2HCl\cdot MEA \rightleftharpoons$$

$$HOCH_2CH_2N=As-NHCH_2CH_2OH + C_2H_2 + HCl\cdot MEA \rightleftharpoons$$



$$+ MEA$$

The first step has an Arrhenius activation energy (Ea) of 16.4 kcal/mole and a preexponential (A) of 3.03×10^{10} $second^{-1}$. The half life at 25°C is 24.4 seconds. Sensitive analyses for residual lewisite in monoethanolamine have offered some difficulties. Thermochemistry of the lewisite-MEA reaction was also studied. The heat of reaction (ΔH) was -41.0 kcal/mole based on lewisite. Products passed the Department of Transportation toxicity test for transportation (less than class B poisons).

---

* Sarver, E. W. Quarterly Progress Report. Research Plan 3394. Defense Research Division. Decontamination of Agents in War Gas Identification Sets. p. 2. 10 June 1974. UNCLASSIFIED Report.

** Epstein, J., Rosenblatt, D. H., Gallacio, A., and McTeague, W. F. Draft Report to Commanding General, US Army Munitions Command, ATTN: AMSMU-MS-CH, Dover, New Jersey. Subject: Chemical Disposal Operations. Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations. 2 October 1972. UNCLASSIFIED Report.

† Epstein, J., Eng, L., Pistritto, J. V., and Jonas, L. Status of Lewisite-Monoethanolamine Investigations. Letter Report from L. Eng, Pollutant Abatement Branch, Environmental Research Division, to Director of Manufacturing Technology, ATTN: SAREA-MT-E/Mr. J. Goheen. 24 January 1977. UNCLASSIFIED Report.

Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Dunnage from the K941-2 and K951-4 Toxic War Gas Sets. 18 March 1975. UNCLASSIFIED Disposition Form.

†† The overall stoichiometry proposed is 4 moles of MEA per mole of lewisite.

Much work has been reported on the reaction of lewisite with sodium hydroxide.* The reaction of lewisite with aqueous sodium hydroxide results in the formation of flammable acetylene; i.e.,

$$ClCH=CH-AsCl_2 + 4NaOH \longrightarrow NaAsO_2 + 3NaCl + C_2H_2\uparrow + 2H_2O$$

The decomposition was found to be essentially instantaneous (i.e., complete in <10 seconds) with a heat of reaction of -102 kcal/mole. An 18% w/v aqueous sodium hydroxide solution containing 0.1% w/v of the surfactant hexadecyltrimethylammonium chloride and 0.2% w/v of the defoamer 2-octanol was recommended for the disposal of 5% of lewisite in chloroform and the agent was assumed to be completely destroyed in 15 minutes.

Lewisite is often accompanied by appreciable amounts (ca 10%-20%) of the vesicant L II, [dichlorovinylchloroarsine $(ClCH=CH)_2-AsCl$], which seems to decompose appreciably more slowly in aqueous sodium hydroxide than does lewisite. While L II in chloroform solutions of lewisite was found to be more resistant than lewisite to aqueous sodium hydroxide, the product solution passed the standard Department of Transportation test.

2.7.3 Analysis.

The recommended assay of lewisite in aqueous sodium hydroxide was somewhat involved** and utilized the reaction of the acetylene produced from an aqueous copper (I) ammonia complex to give a red copper (I) acetylide precipitate. The precipitate was determined either iodometrically (sensitivity of 1 ppm in decontamination solution) or colorimetrically by a copper (II) ammonia complex (12 ppm).

Lewisite was also assayed by gas liquid chromatography after extraction from the aqueous phase by chloroform, but the sensitivity was quite low at 700 ppm.

2.8 Phosgene (CG).

2.8.1 Selected physical properties. The boiling point of phosgene is 8.3°C. Although the solubility of phosgene in water is relatively low, 0.03 gm/100 gm (reference 1, page 65), the compound rapidly decomposes to give water-soluble or gaseous products.

2.8.2 Decontamination.

The most useful mixture for the destruction of phosgene is aqueous sodium hydroxide† (reference 1, page 68).

* Defense Research Branch, Edgwood Arsenal. Disposition Form. Decontamination of Lewisite in Chloroform Contained in the K951-4 War Gas Identification Sets. 1974. UNCLASSIFIED Disposition Form.

** Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Detection of Agents in Decontaminated Toxic War Gas Solutions. Undated. UNCLASSIFIED Disposition Form.

† Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Phosgene in War Gas Identification Sets. 11 June 1974. UNCLASSIFIED Disposition Form.

The reaction of phosgene with water is also complete in less than 20 seconds. However, the low solubility of phosgene in water leads to a requirement for agitation and difficult scrubbing.

Volatility of phosgene (b.p., 8.3°C) would argue for precooling, if a safe neutralization is to be performed, whether by water or by aqueous base. Monoethanolamine was evaluated* as a decontaminant for neat phosgene and its destruction efficiency was found to be comparable to that for aqueous sodium hydroxide.

Residues from the aqueous sodium hydroxide decontamination of phosgene were shown to be nontoxic** and to pass the Department of Transportation test.

$$COCl_2 + 4NaOH \longrightarrow Na_2CO_3 + 2NaCl + 2H_2O$$

The second-order rate constant was given as 10^4 M^{-1} sec^{-1} at 25°C, which indicated that, in 10% aqueous sodium hydroxide, >99% of phosgene would be destroyed in 0.2 millisecond.† The heat of reaction was calculated to be -101 kcal/mole. Because of the low boiling point of CG, it was recommended that the reaction should be run at 0°C with several aqueous sodium hydroxide traps. One reference on the destruction of CW munitions†† reported that CG projectiles were pierced during winter under aqueous sodium and calcium hydroxide in troughs connected to a trickling tower containing the same solution.

2.8.3 Analysis.

A direct method was reported§ for the estimation of CG in aqueous sodium hydroxide, which involved reaction with a mixture of phenyl-1-naphthylamine and p-dimethylaminobenzaldehyde to give a green color at 2.5 ppm or greater.

Several GLC procedures also have been described for phosgene[54,55] with sensitivities of the order of 10^{-3} ppm in air. In addition, the DB-3 reaction[56,57] has proven to be sensitive to <0.1 ppm of phosgene in air.

2.9 Hydrocyanic acid (AC).

2.9.1 Selected physical properties. Hydrocyanic acid has a boiling point of 26°C and it is completely miscible with water.[1] The anhydrous material is subject to explosive polymerization in the presence of bases,[58] but it is relatively stable when mixed with small amounts of acids, such as phosphoric. A jet of AC is easily ignited and it burns with a blue flame.

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Dunnage from the K941-2 and K951-4 Toxic War Gas Sets. 18 March 1975. UNCLASSIFIED Disposition Form.

** Christensen, M. K., Physiotoxicology Branch, Toxicology Division, Biomedical Laboratory. Disposition Form to Chief, Decontamination Research Section, Defense Branch, Chemical Laboratory. Bioassay of Residues from HD/MEA and CG/NaOH Decontamination Trials. 19 February 1974. UNCLASSIFIED Disposition Form.

† Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Phosgene in War Gas Identification Sets. 11 June 1974. UNCLASSIFIED Disposition Form.

†† Sarver, E. W. Quarterly Progress Report. Research Plan 3394. Defense Research Division. Decontamination of Agents in War Gas Identification Sets. p. 2. 10 June 1974. UNCLASSIFIED Report.

§ Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Detection of Agents in Decontaminated Toxic War Gas Solutions. Undated. UNCLASSIFIED Disposition Form.

2.9.2 Decontamination. The method of choice for the destruction of AC involves oxidation by hypochlorite in basic solution (reference 58, page 316),[59*] according to the following equations:

$$2HCN + 5NaOCl + 4NaOH \longrightarrow N_2 + 2Na_2CO_3 + 5NaCl + 3H_2O$$

$$4HCN + 5Ca(OCl)_2 + 8NaOH \longrightarrow 2N_2 + 4CaCO_3 + 8NaCl + 6H_2O + CaCl_2$$

Other workers[60] have reported that cyanogen chloride is an intermediate in the hypochlorite attack of cyanide ion. The cyanogen chloride then hydrolyzes through isocyanate ion to ammonia (then degraded to nitrogen) and carbonate ion. The latter reaction is relatively slow. The reaction may thus be considered to consist of two steps (the first passing through CNCl):

(1) $NaCN + NaOCl \longrightarrow NaOCN + NaCl$

(2) $2NaOCN + 3NaOCl + 2HCl \longrightarrow 5NaCl + 2CO_2 + H_2O + N_2$ or

(2a) $2NaOCN + 3NaOCl + H_2O \longrightarrow 2NaHCO_3 + 3NaCl + N_2$

The second-order rate constant for the reaction was reported to be $2.67 \times 10\ M^{-1}\ sec^{-1}$, the half life was given by the equation $t_{1/2}$ sec $= 2.60 \times 10^{-2}\ (OCl^-)$, and the heat of reaction was estimated to be -215 kcal/mole. The reaction was claimed to give >99.99% destruction of AC. Although no measurements were made of the hypochlorite solution, use of a starch-iodine indicator scrubber showed that less than 0.002% of AC or of cyanogen chloride formed from AC and hypochlorite had escaped from the system. In the laboratory setup employed (see footnote), nitrogen gas was used to slowly transfer the AC to the decontamination solution. On a larger scale, as envisioned for the ECS, problems may arise because of:

a. The high heat of reaction.

b. The low decontaminating capacity of 5% aqueous sodium hypochlorite.

c. The precipitation of calcium carbonate when HTH is used.

d. Evolution of a large volume of nitrogen gas.

e. The possibility of explosive polymerization unless the AC is initially diluted with water.

2.9.3 Analysis. Sensitive methods are available for cyanide ion[58] including a specific ion electrode[61] with a limit of 10^{-6} M. A test paper sensitive to 10 ppm of hydrogen cyanide in air and not subject to chlorine interference contains p-nitrobenzaldehyde and potassium carbonate. (See footnote.) The pyrazolone spectrophotometric method, which involves preliminary conversion of cyanide to cyanogen chloride, can measure down to 0.02 μg/ml of cyanide[62] and is widely used.

* Eng, L., Physical Research Division, Edgewood Arsenal. Disposition Form. The Demilitarization of HCN (AC). 3 May 1974. UNCLASSIFIED Disposition Form.

2.10 Cyanogen chloride (CK).

2.10.1 Selected physical properties.

The boiling point of cyanogen chloride (CK) is 13.8°C and the solubility in water is approximately 6 gm/100 gm with hydrolysis.[63]

$$CNCl + 3NaOH \longrightarrow NaCl + Na_2CO_3 + NH_3$$

The second-order rate constant for the reaction was reported as 6×10^2 M^{-1} min^{-1} and the half life* was given by the equation $t_{1/2} = 69.3$ ms/(OH^-). It was recommended that the decontamination be run at 0°C as the reaction was found to be highly exothermic. As measured with a starch-iodine bubbler mixture, with a limit of 45 μg of cyanogen chloride, destruction of agent was of the order of 99.9996%.

Other workers[64] reported the hydrolysis rate constant to be 1.55×10^{-4} min^{-1} + 272 (OH^-) min^{-1}. Isocyanate (OCN^-) is implicated as an intermediate.

The experimental setup was similar to that for AC, but acid scrubbers were used to trap the ammonia evolved. The caveats mentioned for AC decontamination apply also to that for cyanogen chloride.

2.10.2 Analysis.

The standard spectrophotometric method reported for the analysis of cyanogen chloride was similar to the pyrazolone procedure for cyanide ion[62] except that no initial chlorination was required. The strongly basic decontaminant solution was neutralized with dilute hydrochloric acid and reacted with a reagent containing N-phenyl-1,3-methylpyrazolone in 4-picoline to give a blue color with a sensitivity of 5 ppm of cyanogen chloride.**

2.11 Chloropicrin (PS).

2.11.1 Selected physical properties. The solubility in water of chloropicrin[1] is 0.2 gm/100 gm and the boiling point is 112°C.

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Toxic War Gas Sets. 25 November 1974. UNCLASSIFIED Disposition Form.

** Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Detection of Agents in Decontaminated Toxic War Gas Solutions. Undated. UNCLASSIFIED Disposition Form.

2.11.2 Decontamination.

The two systems that appear to be the most useful for the decontamination of bulk amounts of chloropicrin are alcoholic sodium hydroxide[1,53] and 2-aminoethanol.* The reaction for the former is:

$$CCl_3NO_2 + 5NaOH \longrightarrow 3NaCl + NaNO_2 + NaHCO_3 + 2H_2O;$$

whereas, that for the latter has not been elucidated, although a pseudo-first-order rate constant of 7.47×10^{-2} min^{-1} at 34°C was obtained and a heat of reaction of -160 kcal/mole was calculated. At 50°C, the time required for destruction of >99% of chloropicrin was estimated to be less than 30 minutes.

The destruction of chloropicrin in munitions by alcoholic sodium hydroxide was rapid and was accompanied by a violent reaction that required that the decontamination vats be covered.[53] Substitution of 2-methoxyethanol with its higher boiling point for the ethanol[30] might result in a more easily controlled reaction, but the kinetics and the heat rise would have to be determined.

As mentioned previously,** one potential hazard of the 2-aminoethanol system is that a delayed violent reaction can take place in the presence of chloroform in a closed system. Therefore, for such chloropicrin fills as the CNS mixture with chloroacetophenone and chloroform, it is recommended that the chloroform be destroyed prior to storage by heating at 100°C in an inert atmosphere.

2.11.3 Analysis.

Because of the relatively low solubility of chloropicrin in water, it could be readily extracted by solvents such as chloroform from the 2-aminoethanol solution after dilution with water. Extraction efficiencies were found to be 90%. Analysis of the extract by GLC†,[65] detected down to 5 ppm of chloropicrin in the decontamination solution. The majority of colorimetric methods for chloropicrin are based upon cleavage in basic solution to give the nitrite anion, followed by a diazo coupling reaction. In one procedure,[66] the coupling involved sulfanilic acid and N-(1-naphthyl)ethylenediamine, with a detection of 3 mg/m^3 in air.

Another type of color reaction involved the condensation of chloropicrin with pyridine to give glutaconic dialdehyde,[67] with a reported sensitivity of 0.02 μg/ml.

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of PS in the K953-4 War Gas Identification Sets. 20 March 1975. UNCLASSIFIED Disposition Form.

Defense Research Branch, Edgewood Arsenal. Disposition Form. Decontamination of Chloropicrin (PS) in War Gas Identification Sets. 1975. UNCLASSIFIED Disposition Form.

** Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Decontamination of Toxic War Gas Sets. 18 December 1974. UNCLASSIFIED Disposition Form.

† Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Detection of Agents in Decontaminated Toxic War Gas Solutions. Undated. UNCLASSIFIED Disposition Form.

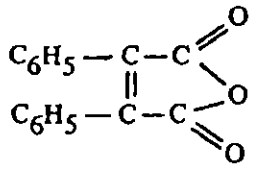
2.12 2-Bromobenzyl cyanide (BBC, formerly CA).

2.12.1 Selected physical properties. 2-Bromobenzyl cyanide is stated to be insoluble or slightly soluble in water.[1] The boiling point is 242°C with decomposition. 2-Bromobenzyl cyanide is unstable in storage except in glass.

2.12.2 Decontamination. Alcoholic sodium hydroxide[1,2,68] has been mentioned in several publications for the destruction of 2-bromobenzyl cyanide although no values for rates or for heats of reaction have been given. If the solution is partly aqueous, then the reaction is presumably:

$$C_6H_5CHBrCN + 2NaOH + H_2O \longrightarrow C_6H_5CHOHCOONa + NaBr + NH_3$$

whereas, if the alcohol is anhydrous, then one of the products formed is diphenylmaleic anhydride



It was observed* that when 2-aminoethanol and 2-bromobenzyl cyanide were mixed, a considerable amount of heat was given off, indicating that a reaction had occurred. This suggests that 2-aminoethanol is a potentially useful decontaminant for 2-bromobenzyl cyanide. However, because more is known about the alcoholic sodium hydroxide system, it remains the one of choice, with the possible substitution of 2-methoxyethanol[30] for the ethanol.

2.12.3 Analysis.

Both colorimetric and GLC methods are available for estimation of trace amounts of 2-bromobenzyl cyanide. The DB-3 method, which is a general one for alkylating agents, is capable of determining amounts of 0.25 μg/ml of the compound; whereas, the GLC technique[69] has a detection level of <3 ng, both from ethanolic solution. As 2-bromobenzyl cyanide is relatively insoluble in water, it should be possible (as it is for chloropicrin) to dilute the decontamination solution with water or with aqueous sodium chloride, followed by extraction with a solvent such as chloroform, to recover intact agent.

In addition to the above methods, it should be possible to check the efficiency of destruction of 2-bromobenzyl cyanide by a reported TLC technique employing a DB-3 spray capable of detecting 25 μg of the compound in an aqueous or an organic solvent.

2.13 Miscellaneous agents. In addition to the aforementioned liquid agents, which are the ones most likely to be present as unknowns in unmarked munitions, a number of other compounds,[1-3] although much less likely to be encountered, should be mentioned.

* Yurow, H. W., Chemical Systems Laboratory. Unpublished results. 13 June 1980.

2.13.1 Arsenicals. There are a number of lesser known arsenic-containing agents related to lewisite.[1] They are all relatively insoluble in water (ca 0.1 gm/100 gm), but they can be readily decontaminated, as is lewisite by aqueous sodium hydroxide; e.g.,

$$CH_3AsCl_2 + 2NaOH \longrightarrow CH_3AsO + 2NaCl + H_2O$$

Included are methyl dichloroarsine (MD, CH_3AsCl_2) — boiling point, 132-133°; ethyl dichloroarsine (ED, $C_2H_5AsCl_2$) — boiling point, 156°C; phenyl dichloroarsine (PD, $C_6H_5AsCl_2$) — boiling point, 255-257°C; and diphenylchloroarsine [DA, $(C_6H_5)_2AsCl$] — boiling point, 333°C.

2.13.2 Diphosgene (DP). Also known as trichloromethyl chloroformate ($ClCOOCCl_3$), the compound is relatively insoluble in water and boils at 128°C. It is readily decomposed by aqueous sodium hydroxide, $ClCOOCl_3 + 8NaOH \longrightarrow 4NaCl + 2Na_2CO_3 + 4H_2O$. Diphosgene can be detected by all of the procedures used for phosgene.

2.13.3 Smoke agents.[2] The two most common liquid ones are chlorosulfonic acid (FS, $ClSO_3H$) and titanium tetrachloride (FM, $TiCl_4$). Both can be decontaminated by treatment with water followed by neutralization of the acid with aqueous sodium hydroxide.

2.13.4 HL mixture. For this combination munition fill (lewisite and mustard), the recommended decontaminant would be 2-aminoethanol (see reference 2).

3. BEST CHOICE DECONTAMINANT FOR UNKNOWN FILLS

Two properties of CW agents are of primary importance in their decontamination:

(a) They are almost invariably electrophilic compounds.

(b) Many of them have only slight solubility in water. Therefore, the best general reagent for their destruction should be a strong nucleophile and a good general solvent for organic compounds. One decontaminant that seems to be effective for a wide variety of agents is 2-aminoethanol,* which has been previously described in this report. Taking account of the side reaction with chloroform, it is generally superior to bleach slurries or to sodium hydroxide in water or in various solvent mixtures, which are the other two widely used multiagent decontaminants.

Incineration is also an excellent choice as a multiagent detoxification method and efficiencies have been reported for a number of agents.[70]

4. RECOMMENDED DECONTAMINANTS FOR VARIOUS AGENTS IN THE ECS SYSTEM

Based upon data described previously in this report, the following decontaminants have been recommended for the agents of interest:

(a) GA.

Aqueous sodium hydroxide is recommended unless aluminum is present; then aqueous sodium carbonate is preferred to avoid formation of hydrogen. The cyanide produced can be destroyed, if necessary,

* Crumb, E. A., Edgewood Arsenal. Disposition Form to Director of Manufacturing Technology. Use of MEA as Decontaminant for Agents in Kits. 25 November 1974. UNCLASSIFIED Disposition Form.

by subsequent treatment with aqueous calcium hypochlorite. Heat evolution should not present a problem as the ΔH is relatively low.

(b) GB.

Aqueous sodium hydroxide is recommended. The comments for GA regarding aluminum and heat evolution also apply for GB, as well as for GD below.

(c) GD.

Sodium hydroxide in a mixture of water and 2-methoxyethanol is the decontaminant of choice. The organic solvent is needed to give homogeneity.

(d) VX.

At present, no system can be recommended for ECS. However, aqueous calcium hypochlorite or Fichlor would be suitable with strong agitation if a reliable analytical method were to be developed. Fichlor is expected to react in a similar manner to that of HTH. The analysis of residual VX in dilute HTH brine is described in reference 36. Additional effort would be required to ensure that the method vigorously meets requirements.

(e) HD.

If temperature can be reasonably closely controlled in the ECS system, then 2-aminoethanol is the preferred reagent, as the reaction is homogeneous. If not, then calcium hypochlorite is suggested with the requirements of strong agitation and representative sampling.

(f) HN-1, HN-2, HN-3.

At present, no system can be recommended. However, the use of 2-aminoethanol appears to be promising, pending a study of the thermochemistry of the reaction.

(g) L.

The suggested decontaminant is 2-aminoethanol. Caution should be exercised, as acetylene is formed.

(h) CG.

Aqueous sodium hydroxide is the reagent of choice. Because of the low boiling point of phosgene, provisions for cooling may be required.

(i) AC.

Aqueous calcium hypochlorite is recommended, following an initial dilution with water, to avoid explosive polymerization.

(j) CK.

Aqueous sodium hydroxide and strong cooling are recommended for this compound.

(k) PS.

Because of insufficient data, no decontaminant can be recommended. However, the most promising appears to be sodium hydroxide in a water and 2-methoxyethanol mixture.

(l) BBC.

As with chloropicrin, insufficient data prevent a selection, but sodium hydroxide in aqueous 2-methoxyethanol shows promise.

LITERATURE CITED

1. Sartori, M. The War Gases. D. Van Nostrand, New York, New York. 1940.

2. Defense CW Manual, FTP 222. United States Navy Department, Washington, DC. 1944.

3. Civil Defense Technical Bulletin, TB-11-28. Chemical Warfare Agents of Special Significance to Civil Defense. Government Printing Office, Washington, DC. January 1957.

4. Larsson, L. The Alkaline Hydrolysis of Two Sarin Analogues of Tabun. Acta Chem. Scand. *12*, 783 (1958).

5. Neale, E. Porton Technical Paper No. 339. The Thermochemistry of Organic Phosphorus Compounds, Part III. Determination of Some Heats of Formation by Reaction Calorimetry and the Estimation of Bond Energy Terms. November 1953. UNCLASSIFIED Report.

6. Epstein, J., and Rosenblatt, D. H. EASP 1200-12. Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations. January 1973. UNCLASSIFIED Report.

7. Larsson, L. The Hydrolysis of Dimethylamidoethoxyphosphoryl Cyanide (Tabun). Acta Chem. Scand. *1*, 306 (1953).

8. Davis, G. T., Block, F., Gorrell, J. D., and Epstein, J. EC-TR-76101. Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components. March 1977. UNCLASSIFIED Report.

9. Rinehart, D., and Deiner, A. ARCSL-TR-77030. Method of Analysis for Determination of Isopropylmethylphosphonofluoridate (GB) in Carbonate Brines. July 1977. UNCLASSIFIED Report.

10. Marsh, D. J., and Neale, E. The Reaction of Alkaline Hydrogen Peroxide with Certain Acid Halides and Anhydrides in the Presence of Benzidine-Type Bases. J. Appl. Chem. *8*, 394 (1958).

11. Sass, S., Ludemann, W. D., Witten, B., Fischer, V., Sisti, A. J., and Miller, J. I. Colorimetric Determination of Certain Organophosphorus Compounds and Acylating Reagents. Anal. Chem. *29*, 1346 (1957).

12. Bassett, M. C., Herd, R. E., and Woolridge, A. L. EATR 4117. An Improved Fluorometric Method of Analysis of VX in Field-Test Samples. July 1967. UNCLASSIFIED Report.

13. Crabtree, E. V., and Sarver, E. W. EC-SP-76021. Review of Analytical Procedures for GB, VX and Their Degradation Products. January 1977. UNCLASSIFIED Report.

14. Matousek, J., Cerman, J., Horak, O., and Kovar, V. A New Fluorometric Method for Determination of Submicrogram Amounts of Cholinesterase Inhibitors. Chem. Zvesti. *22*, 184 (1968). C. A. *64*, 641j (1968).

15. Stutz, M., and Sass, S. EC-TR-76091. Collection and Sampling of Materials and Preparation for Identification and Other Analysis. June 1977. UNCLASSIFIED Report.

16. Larsson, L. The Alkaline Hydrolysis of Isopropyl Methyl-Phosphoryl-Fluoride and Some Analogs. Acta Chem. Scand. *11*, 1131 (1957).

17. Edwards, B. A. DPG-SS-C130A. Caustic Immersion Demilitarization of M55 Rocket Residue. Dugway Proving Ground, Dugway, Utah. February 1974. UNCLASSIFIED Report.

18. Block, F., and Davis, G. T. ARCSL-TR-79002. Survey of Decontamination Methods Related to Field Decontamination of Vehicles and Materiel (Abridged). October 1978. UNCLASSIFIED Report.

19. Larsson, L. Studies on the Chemical Reactivity of Organic Phosphorus Compounds. Svensk. Kem. Tidskr. *70*, 405 (1958).

20. Mankowich, K., Butcosk, A. F., Robbins, R., Roberts, W. B., West, A. L., and Love, S. EASP 300-5. History of Research and Development of the Chemical Warfare Service Through 1945. Decontamination of Chemical Agents. Part II. September 1970. UNCLASSIFIED Report.

21. Yurow, H. W. ARCSL-SP-80032. Decontamination Methods for HD, GB, and VX – A Literature Survey. April 1981. UNCLASSIFIED Report.

22. Dismukes, E. B., and Barrett, W. J. AFATL-TR-68-77. All-Purpose Chemical/Biological (CB) Decontaminant. Contract AF08-(675)-5410. Southern Research Institute, Birmingham, Alabama. June 1968. UNCLASSIFIED Report.

23. Epstein, J., Davis, G. T., Demek, M. M., Eng, L., Gorrell, J. D., Pistritto, J. V., Jones, J. T., Richmond, J. A., Sarver, E. W., Schiff, L. J., Block, F., Sommer, H. Z., and Daasch, L. W. EC-TR-76009. On the Mechanism of GB Formation in the Spray Drying of GB Contaminated Brine Solutions. November 1975. UNCLASSIFIED Report.

24. Epstein, J., Davis, G. T., Eng, L., and Demek, M. M. Potential Hazards Associated with Spray Drying Operations. Environ. Sci. Technol. *11*, 70 (1977).

25. Davis, P. M., Brooks, M. L., Mason, T., and Sass, S. EC-TR-76079. Chemical and Thermal Methods for Analysis of GB Demilitarization Brines and Spray-Dried Salts. February 1977. UNCLASSIFIED Report.

26. Demek, M. M., Davis, G. T., Dennis, W. H., Hill, A. L., Farrand, R. L., Musselman, N. P., Mazza, R. J., Levine, W. D., Rosenblatt, D. H., and Epstein, J. EATR 4417. Behavior of Chemical Agents in Seawater. August 1970. UNCLASSIFIED Report.

27. Epstein, J. Properties of GB in Water. J. Am. Water Works Assoc. *66*, 31 (1974).

28. Thomas, G. W. DRCPM-DRD-TR-72015. Demil Plan Operation of the CAMDS at Tooele Army Depot. Inclosure No. 10. Agent Destruction System Testing and Reliability Data. March 1977. UNCLASSIFIED Report.

29. Fisher, T. L., Steger, R. J., Parker, G. A., and Sass, S. EC-TR-76080. Gas Chromatographic Methods for the Analysis of Trace Quantities of GB and Associated Compounds. September 1976. UNCLASSIFIED Report.

30. Davis, P. M., Kipp, R. L., Brooks, M. E., and Duggan, M. L. ARCSL-TR-79004. Decontaminating Solution for the Disposal of Identification and Training Sets. April 1979. UNCLASSIFIED Report.

31. Benson, J. H., Valis, R. J., Kramer, S. R., Heminger, David M., Hildebrandt, H. F., and Berenthien, T. C. EM-TR-73070. Laboratory and Pilot Scale Detoxification of VX in Acidic Media Using Chlorine Gas. May 1974. UNCLASSIFIED Report.

32. Bauer, V. E., Demek, M. M., Corey, G. G., and Epstein, J. CWLR 2231. Chlorination of VX in Dilute Aqueous Solution at 25°C. August 1958. UNCLASSIFIED Report.

33. Hedley, W. H., Richardson, G. A., Early, D. E., Moscowitz, C. M., and Rezvik, R. B. ARCSL-CR-77003. Disposal of Detoxified Chemical Agents. Contract DAAA15-74-C-0073. Monsanto Research Corporation, Dayton, Ohio. March 1975. UNCLASSIFIED Report.

34. Childers, C. D. Technical Memorandum, W-15167. Decontamination of Bulk Quantities of VX with NaOH-Aqueous Solution. U.S. Naval Weapons Laboratory, Dahlgren, Virginia. August 1967. UNCLASSIFIED Report.

35. Michel, H. O., Epstein, J., Plapinger, R., and Fleisher, J. CWL Technical Memorandum 11-2. EA 2192 (U) (Abbreviated Title). March 1970. UNCLASSIFIED Report.

36. US Army Toxic and Hazardous Materials Agency OM 3-6640-100-20. Operation and Maintenance Manual for the Transportable Chemical Laboratory of the Drill and Transfer System. October 1980. UNCLASSIFIED Report.

37. Brankowitz, W. R. ARCSL-TR-77051. Demilitarization of Mustard Agent (HD) at Fort McClellan, Alabama. April 1978. UNCLASSIFIED Report.

38. Colburn, E. F. Monitoring the Disposal of Hazardous Materials. Conference Proceedings, 4th Joint Conference on Sensing of Environmental Pollutants. New Orleans, Louisiana. November 6-11, 1977. pp 489-492. UNCLASSIFIED Report.

39. Toxic and Hazardous Industrial Chemicals Safety Manual. The International Technical Information Institute, Tokyo, Japan. 1976.

40. Helferich, O. B., and Reid, E. E. Reactions and Derivatives of β,β'-Dichloroethyl Sulfide. J. Am. Chem. Soc. *42*, 1208 (1920).

41. Smith, D. W., Taylor, M. C., Young, R., and Stephens, T. Accelerating Rate Calorimetry. Am. Lab. *12*, 51 (1980).

42. Hurd, C. D., Moe, D. A., and Starke, A. C. Some Observations Regarding Chloroethyl and Chlorovinyl Sulfides. Int. J. Sulfur Chem., Part A, *2*, No. 2, 113 (1972).

43. Lawson, W., and Dawson, T. Chlorination of β,β'-Dichloroethyl Sulfide. J. Am. Chem. Soc. *49*, 3119, 3125 (1927).

44. Mann, F. G., and Pope, W. J. Production and Reactions of β,β'-Dichlorodiethyl Sulphide. J. Chem. Soc. *121*, 594 (1922).

45. Davies, J.S.H., and Oxford, A. E. Formation of Sulphonium Chlorides and of Unsaturated Substances by the Action of Water and of Aqueous Alcoholic Potash on β,β'-Dichloroethyl Sulphide. J. Chem. Soc., 224 (1931).

46. Fisher, T. L., Jaskot, R., and Sass, S. EATR 4321. Trace Estimation and Differentiation of Some Mustards Employing GLC. July 1969. UNCLASSIFIED Report.

47. Epstein, J. Use of γ-(4-Nitrobenzyl)pyridine as Analytical Reagent for Ethyleneimine and Alkylating Agents. Anal. Chem. *27*, 1435 (1955).

48. Golumbic, C., Fruton, J. S., and Bergmann, M. Chemical Reactions of the Nitrogen Mustard Gases. J. Org. Chem. *11*, 518-35 (1946).

49. Gurin, S., Delluva, A. M., and Crandall, D. I. Chemical Reactions of Nitrogen Mustard Gases. I. Reactions of Methyl-Bis(β-Chloroethyl)amine with Hexamethylenetetramine. J. Org. Chem. *12*, 606 (1947).

50. Price, C. C., Kasbas, G,, and Nakata, I. Some Amino and Ammonio Nitrogen Mustard Analogs. J. Med. Chem. *8*, 650 (1965).

51. Cohen, B., and Van Artsdalen, E. R. Studies on the Kinetics of the β-Chloroethylamines and Their Products in Dilute Aqueous Solution. N.D.R.C., OSRD No. 3557. UNCLASSIFIED Report. 1 May 1944. Cf, Cohen, B., Van Artsdalen, E. R., and Harris, J. Reaction Kinetics of Aliphatic Tertiary β-Chloroethylamines in Dilute Aqueous Solution, I. The Cyclization Process. J. Am. Chem. Soc. *70*, 281 (1948).

52. Hunt, C. E., and Philips, F. S. Acute Pharmacology of Methylbis(2-chloroethyl)amine (HN-2). J. Pharmacol. Exp. Ther. *95*, 131 (1949).

53. Scholz, S. Erfahrungen bei der Vernichtung alter Kampstoffmunition. Explosivstoffe *11*, 159, 181 (1963).

54. Sass, S., Parker, G. A., and Fisher, T. L. EC-TR-76047. Gas Chromatographic Method for the Determination of Phosgene in Effluent Air. August 1976. UNCLASSIFIED Report.

55. Dahlberg, J. A., and Kihlman, I. B. Gas Chromatographic Determination of Chlorinated Acetyl Chlorides and Phosgene Present in Air in Very Low Concentrations. Acta Chem. Scand. *24*, 644 (1970).

56. Noweir, M., and Pfister, E. A. Improved Method for Determination of Phosgene in Air. Am. Ind. Hyg. Assoc. J. *32*, 163 (1971).

57. Dixon, B. E., and Hands, G. C. A Field Method for the Determination of Phosgene. Analyst *84*, 463 (1959).

58. Kirk-Othmer Encyclopedia of Chemical Technology. 3d Edition. Vol. 7. John Wiley and Sons, New York, New York. 1979.

59. Blakely, C. P., and Thomas, T. K. Instrumentation for Water Pollution Monitoring. Environ. Sci. Technol. *7*, 1008 (1973).

60. Gladysheva, A. I., Fedorina, G. N., Abliisova, I. G., Gus'kov, V. A., and Demidkina, T. A. Mechanism and Kinetics of Oxidation of Cyanides by Active Chlorine. Uch. Zap. Tsentr. Nauchno Issled. Inst. Olovyannoi Promsti. *3* (1969) [Cf. *CA. 76*, 28188k (1972)].

61. Vesely, J., Weiss, D., and Stulik, K. Analysis with Ion Selective Electrodes. p. 152. John Wiley and Sons, New York, New York. 1978.

62. Epstein, J. Estimation of Microquantities of Cyanide. Anal. Chem. *19*, 272 (1947).

63. Handbook of Chemistry and Physics. 41st Ed. Chemical Rubber Publishing Company, Cleveland, Ohio. 1959.

64. Bailey, P. L., and Bishop, E. Hydrolysis of Cyanogen Chloride. J. Chem. Soc. (Dalton), 912 (1973).

65. Berck, B. Determination of Fumigant Gases by Gas Chromatography. J. Agric. Food Chem. *113*, 373 (1965).

66. Feinsilver, L., and Oberst, F. W. Microdetermination of Chloropicrin Vapor in Air. Anal. Chem. *25*, 820 (1953).

67. Fournier, R. M., and Person, M. Colorimetric Microdetermination of Chloropicrin in Air. Chim. Anal. *39*, 263 (1957).

68. Jacobs, M. B. War Gases, Their Identification and Decontamination. Interscience Publishers, New York, New York. 1942.

69. Martin, J. J., Fisher, T. L., and Sass, S. EATR 4086. Soil Stability of CA and CN and Vapor Concentration of CA under Static Conditions. Analytical Methods for the Determination of Trace Quantities of the Agents. April 1967. UNCLASSIFIED Report.

70. Brooks, M. E., and Davis, P. M. EC-TR-77023. Demilitarization of Identification Kits by Incineration. June 1977. UNCLASSIFIED Report.

Table A-1. Thermochemical Data for Disposal Reactions

Agent	Decontaminant	Heat of reaction, T	Temperature rise[a] calculation already performed
		kcal/mole	
GA	Sodium hydroxide	-10.1	No
GB	Sodium hydroxide	-44.4	No
GB	10% Sodium carbonate	-22	Yes[b]
VX	Alkaline hypochlorite	Approx. -700	Yes[b,c]
VX	Acidic chlorination	Highly exothermic	No
VX	Sodium dichloroisocyanurate	Highly exothermic	No
HD (mustard)	Alkaline hypochlorite	Highly exothermic	No
HD (mustard)	Monoethanolamine (MEA)	-40 (50°C)[d]	No[e]
L (lewisite)	Monoethanolamine (MEA)	-41	No
L (lewisite)	Sodium hydroxide	-102	No
CG (phosgene)	Sodium hydroxide	-101	No
AC (hydrogen cyanide)	Alkaline bleach	-215	No
PS (chloropicrin)	Monoethanolamine	-160	No

[a] Temperature rises can be calculated for reactions with 10% HTH using a heat capacity of 1.1 cal deg^{-1} $mole^{-1}$ and assuming a certain ratio of the decontamination solution (in excess) to the agent, knowing the heat of reaction.

[b] Thermal tests on rockets also were performed.

[c] Heat rise, $\Delta T\ (^{\circ}C) = \frac{\text{moles VX} \times (275)}{\text{gallons of 10\% HTH}}$.

[d] The heat is temperature dependent and also has been determined for other temperatures than that cited in the above table.

[e] Temperature rises may be calculated for given weight ratios of reactants using heat capacities of products varying from 0.802 cal deg^{-1} gm^{-1} at 50°C to 0.823 cal deg^{-1} gm^{-1} at 86°C.

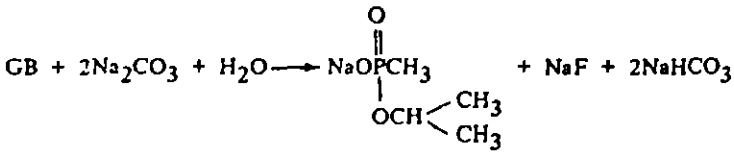
Table A-2. Rates, Gravimetric Ratios, and Capacities for Disposal Reactions

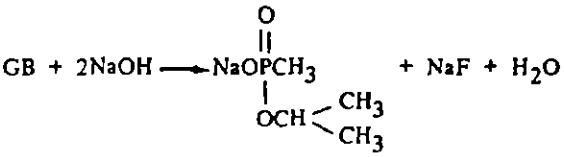
Agent	Decontaminant	Temperature	Half life	Active ingredient gravimetric ratio*	Decontaminant capacity
					gm/gm**
GA	Water (pH 9.5)	25°C	35 Minutes	–	–
GA	Seawater	25°C	175 Minutes	–	–
GB	10% Sodium carbonate	25°C	8.5 Seconds	1.51	0.066
GB	Seawater	25°C	8 Hours	–	–
GB	Soil	15°C	2.5-24 Hours	–	–
GB	Water (pH 10)	25°C	~4 Minutes	–	–
GB	5% Sodium hydroxide	25°C	<0.8 Second	0.571	0.0875
GB	DS-2	25°C	Instantaneous	Not established	
GB	5% Bleach (alkaline)	25°C	Instantaneous	~1.06	~0.047
VX	Bleach slurry (10% HTH)	25°C	~70 Seconds	~4.83	0.0207
VX	Acidic bleach (pH 4)	25°C	1.2 Minutes	0.798 (Cl_2)	Concentration dependent
VX	Water (pH 14)	25°C	1.3 Minutes	–	–
VX	Seawater	25°C	~Years	–	–
VX	Soil	–	~1 Day (95% in 10 days)	–	–
VX	DS-2	25°C	Seconds	~0.300	0.067
H, HD	Monoethanolamine (5:1)	52°C	16 Minutes	1.150	~0.2 at 5:1
HN-1	Seawater (pH 7.88)	25°C	1.5 Minutes	–	–
HN-1	Dilute sodium hydroxide	18°C	12 Minutes	–	–
HN-1	Monoethanolamine (~10% chloroform)	25°C	35 Minutes	1.876	~0.2 at 5:1
L	Water	25°C	Very fast (toxic products)	–	–
L	Seawater	25°C	Instantaneous	–	–
L	Monoethanolamine (MEA)	25°C	24 Seconds	1.176	0.2 at 5:1
L	5% Aqueous sodium hydroxide	25°C	Instantaneous	0.964	0.052 (5%)
CG (phosgene)	Water	25°C	<20 Seconds	–	–
CG (phosgene)	10% Sodium hydroxide	25°C	<<0.2 Milliseconds	1.623	0.0616
AC (hydrocyanic acid)	(10% HTH) Alkaline hypochlorite	25°C	$\frac{2.6 \times 10^{-2}}{(OCl^-)}$ Seconds	17.92	0.0056
CK (cyanogen chloride)	Aqueous sodium hydroxide	25°C	$\frac{69.2}{(OH^-)}$ Milliseconds	1.95	0.051 10% NaOH
PS (chloropicrin)	Monoethanolamine (MEA)	34°C	~10 Milliseconds	–	–
PS (chloropicrin)	10% NaOH	–	–	1.216	0.0822

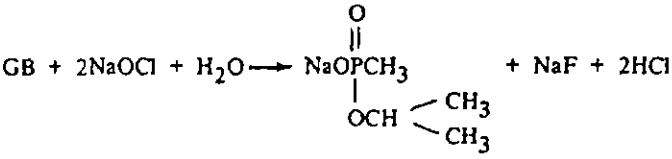
* Ratio of active ingredient required to agent destroyed.

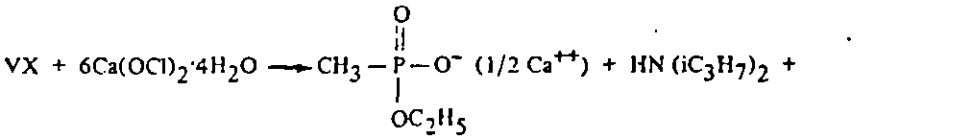
** Grams of agent destroyed per gram of full decontamination formulation.

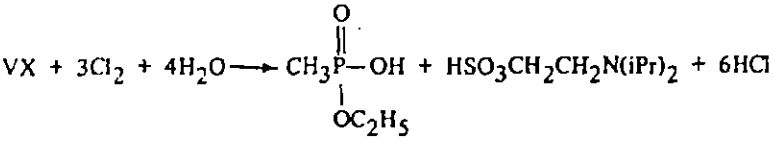
Table A-3. Reaction Equations Used for Calculations in Table 2

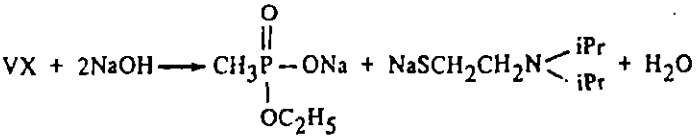


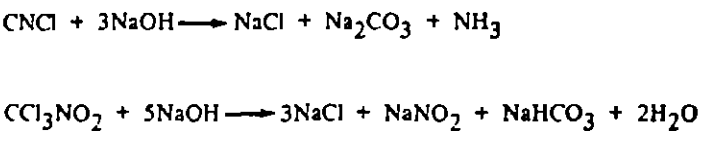












Note: In some of these reactions, hypochlorite was assumed to buffer the reaction in the absence of other added bases.

DISTRIBUTION LIST 7

Names	Copies
CHEMICAL SYSTEMS LABORATORY	
ATTN: DRDAR-CLB	1
ATTN: DRDAR-CLB-C	1
ATTN: DRDAR-CLB-PO	1
ATTN: DRDAR-CLB-R	1
ATTN: DRDAR-CLB-R(A)	1
ATTN: DRDAR-CLB-T	1
ATTN: DRDAR-CLC-B	1
ATTN: DRDAR-CLF	1
ATTN: DRDAR-CLJ-R	2
ATTN: DRDAR-CLJ-L	2
ATTN: DRDAR-CLJ-M	1
ATTN: DRDAR-CLJ-P	1
ATTN: DRDAR-CLN	1
ATTN: DRDAR-CLT	1
ATTN: DRDAR-CLW-C	1
ATTN: DRDAR-CLW-P	1
ATTN: DRDAR-CLW-E	1
ATTN: DRDAR-CLY-A	1
ATTN: DRDAR-CLY-R	4
ATTN: DRDAR-CLR-I	1
COPIES FOR AUTHOR(S) Research Division	2
RECORD COPY: DRDAR-CLB-A	1
DEPARTMENT OF DEFENSE	
Mr. Joseph F. Campbell, Jr. Office of Management and Budget/EXOP New Executive Office Building Rm 10002 726 Jackson Place, N.W. Washington, DC 20503	1
Defense Technical Information Center ATTN: DTIC-DDA-2 Cameron Station, Building 5 Alexandria, VA 22314	2
Director Defense Intelligence Agency ATTN: DB-4G1 Washington, DC 20301	1
Commander USASED, USAINSCOM ATTN: IAFM-SED-III Fort Meade, MD 20755	1
DEPARTMENT OF THE ARMY	
HQDA ATTN: DAMO-NCC ATTN: DAMO-NC/COL Robinson WASH DC 20310	1 1
Federal Emergency Management Agency Office of Research/NPP ATTN: David W. Bensen Washington, DC 20472	1
HQ DA Office of the Deputy Chief of Staff for Research, Development & Acquisition ATTN: DAMA-CSS-C Washington, DC 20310	1
HQ Sixth US Army ATTN: AFKC-OP-NBC Presidio of San Francisco, CA 94129	1
Commander DARCOM, STITEUR ATTN: DRXST-STI Box 48, APO New York 09710	1
Commander USASTCFEO ATTN: MAJ Mikeworth APO San Francisco 96328	1
HQ, 5th Infantry Division (Mech) ATTN: Division Chemical Officer Fort Polk, LA 71459	1

Army Research Office
ATTN: DRXRO-CB (Dr. R. Ghirardelli) 1
P.O. Box 12211
Research Triangle Park, NC 27709

OFFICE OF THE SURGEON GENERAL

Commander
US Army Medical Bioengineering Research and Development Laboratory
ATTN: SGRD-UBD-AL, Bldg 568 1
Fort Detrick, Frederick, MD 21701

Commander
USA Medical Research Institute of Chemical Defense
ATTN: SGRD-UV-L 1
Aberdeen Proving Ground, MD 21010

Commandant
Academy of Health Sciences, US Army
ATTN: HSHA-CDH 1
ATTN: HSHA-IPM 2
Fort Sam Houston, TX 78234

US ARMY MATERIEL DEVELOPMENT AND READINESS COMMAND

Commander
US Army Materiel Development and Readiness Command
ATTN: DRCLDC 1
ATTN: DRCSF-P 1
5001 Eisenhower Ave
Alexandria, VA 22333

Commander
US Army Toxic & Hazardous Materials Agency
ATTN: DRXTH-ES 1
Aberdeen Proving Ground, MD 21010

Director
Human Engineering Laboratory
ATTN: DRXHE-IS (Barnes) 1
Aberdeen Proving Ground, MD 21005

Commander
US Army Foreign Science & Technology Center
ATTN: DRXST-MT3 1
220 Seventh St., NE
Charlottesville, VA 22901

Director
US Army Materiel Systems Analysis Activity
ATTN: DRXSY-MP 1
ATTN: DRXSY-CA (Mr. Metz) 2
Aberdeen Proving Ground, MD 21005

Commander
US Army Missile Command
Redstone Scientific Information Center
ATTN: DRSMI-RPR (Documents) 1
Redstone Arsenal, AL 35809

Director
DARCOM Field Safety Activity
ATTN: DRXOS-C 1
Charlestown, IN 47111

Commander
US Army Natick Research and Development Laboratories
ATTN: DRDNA-O 1
ATTN: DRDNA-IC 1
ATTN: DRDNA-ICAA 1
ATTN: DRDNA-ITF (Dr. Roy W. Roth) 2
Natick, MA 01760

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND

Commander
US Army Armament Research and Development Command
ATTN: DRDAR-LCA-L 1
ATTN: DRDAR-LCU-CE 1
ATTN: DRDAR-NC (COL Fields) 3
ATTN: DRDAR-SCM 1
ATTN: DRDAR-TDC (Dr. D. Gyorog) 1
ATTN: DRDAR-TSS 2
ATTN: DRCPM-CAWS-AM 1
Dover, NJ 07801

Commander
ARRADCOM
ATTN: DRDAR-QAC-E 1
Aberdeen Proving Ground, MD 21010

Commander
USA Technical Detachment 1
US Naval EOD Technology Center
Indian Head, MD 20640

US ARMY ARMAMENT MATERIEL READINESS COMMAND

Commander
US Army Armament Materiel Readiness Command
ATTN: DRSAR-ASN 1
ATTN: DRSAR-IRW 1
ATTN: DRSAR-LEP-L 1
ATTN: DRSAR-SF 1
Rock Island, IL 61299

Commander
USA ARRCOM
ATTN: DRSAR-MAY-M 1
Aberdeen Proving Ground, MD 21010

Commander
US Army Dugway Proving Ground
ATTN: Technical Library (Docu Sect) 1
Dugway, UT 84022

US ARMY TRAINING & DOCTRINE COMMAND

Commandant
US Army Infantry School
ATTN: CTDD, CSD, NBC Branch 1
Fort Benning, GA 31905

Commandant
US Army Missile & Munitions Center and School
ATTN: ATSK-CM 1
ATTN: ATSK-TME 1
Redstone Arsenal, AL 35809

Commander
US Army Logistics Center
ATTN: ATCL-MG 1
Fort Lee, VA 23801

Commandant
US Army Chemical School
ATTN: ATZN-CM-C 1
ATTN: ATZN-CM-AD 2
ATTN: ATZN-CM-TPC 2
Fort McClellan, AL 36205

Commander
USAAVNC
ATTN: ATZQ-D-MS 1
Fort Rucker, AL 36362

Commander
US Army Infantry Center
ATTN: ATSH-CD-MS-C 1
Fort Benning, GA 31905

Commander
US Army Infantry Center
Directorate of Plans & Training
ATTN: ATZB-DPT-PO-NBC 1
Fort Benning, GA 31905

Commander
USA Training and Doctrine Command
ATTN: ATCD-N 1
Fort Monroe, VA 23651

Commander
US Army Armor Center
ATTN: ATZK-CD-MS 1
ATTN: ATZK-PPT-PO-C 1
Fort Knox, KY 40121

Commander
USA Combined Arms Center and Fort Leavenworth
ATTN: ATZL-CAM-IM 1
Fort Leavenworth, KS 66027

US ARMY TEST & EVALUATION COMMAND

Commander
US Army Test & Evaluation Command
ATTN: DRSTE-CT-T 1
Aberdeen Proving Ground, MD 21005

DEPARTMENT OF THE NAVY

Chief of Naval Research
ATTN: Code 441 — 1
800 N. Quincy Street
Arlington, VA 22217

Officer-in-Charge
Marine Corps Detachment — 1
Naval Explosive Ordnance Disposal
Technology Center
Indian Head, MD 20640

Commander
Naval Surface Weapons Center
Code G51 — 1
Dahlgren, VA 22448

Chief, Bureau of Medicine & Surgery
Department of the Navy
ATTN: MED 3C33 — 1
Washington, DC 20372

Commander
Naval Air Development Center
ATTN: Code 2012 (Dr. Robert Helmbold) — 1
Warminster, PA 18974

US MARINE CORPS

Commanding General
Marine Corps Development and
Education Command
ATTN: Fire Power Division, D091 — 1
Quantico, VA 22134

DEPARTMENT OF THE AIR FORCE

ASD/AESD — 1
Wright-Patterson AFB, OH 45433

HQ AFSC/SDZ — 1
ATTN: CPT D. Riedlger
Andrews AFB, MD 20334

HQ, AFSC/SDNE — 1
Andrews AFB, MD 20334

HQ, AFSC/SGB — 1
Andrews AFB, DC 20334

AFAMRL/HE
ATTN: Dr. Clyde Repioggie — 1
Wright-Patterson AFB, OH 45433

USAF TAWC/THL — 1
Eglin AFB, FL 32542

USAF SC
ATTN: AD/YQ — 1
ATTN: AD/YQO (MAJ Owens) — 1
Eglin AFB, FL 32542

USAFSAM/VN
Deputy for Chemical Defense
ATTN: Dr. F. Wesley Baumgardner — 1
Brooks AFB, TX 78235

AFAMRL/TS
ATTN: COL Johnson — 1
Wright-Patterson AFB, OH 45433

AMD/RDE — 1
Brooks AFB, TX 78235

AMD/RDTK
ATTN: LTC T. Kingery — 1
Brooks AFB, TX 78235

OUTSIDE AGENCIES

Battelle, Columbus Laboratories
ATTN: TACTEC — 1
505 King Avenue
Columbus, OH 43201

Toxicology Information Center, JH 652
National Research Council — 1
2101 Constitution Ave., NW
Washington, DC 20418

US Public Health Service
Center for Disease Control
ATTN: Lewis Webb, Jr. — 1
Building 4, Room 232
Atlanta, GA 30333

END

DATE
FILMED

1—83

DTIC

REVIEW OF INFORMATION/INFORMATION MATERIALS PAO-99-264

1 AUTHOR/COTR. Extension Office Symbol
Harvey W. Yurow, Ph.D

2. MATERIAL CLASSIFICATION
(Circle one): (UNCL) CONF SECRET
Distribution Limited

3. TYPE OF MATERIAL.

X Technical Report
__ Technical Note
__ Oral Presentation
__ Poster Session
__ Contractor Report
__ Special Publication
__ Abstract
__ Other

4. FUNDING CATEGORY: (Circle one)

6.1 6.2 6.3. 6.4
6.5 Customer Other
(if customer, please identify)

5. TITLE: CRDEC-SP-88020 Decontamination of Chemical Agents BA, GB, GD, HD, L, and VX A Literature Survey (1918-1987)

6. TYPE OF RELEASE.

X UNLIMITED DISTRIBUTION. Statement A (Public Release)
__ LIMITED DISTRIBUTION. Select statement below (check one only) and give applicable reason (see chart on page 4 of this form)
__ B - U.S. Government agencies only
__ C - U.S. Government agencies and their contractors only
__ D - DoD and U.S. DoD contractors only
__ E - DoD Components only
__ F - Further dissemination only as directed by Cdr, Chemical and Biological Defense Command (CBDCOM) or his designee.
__ X - U.S. Government agencies and private individuals or enterprises eligible to obtain export-controlled technical data

REASON: Utah Chemical Agent Rule Repository

__ Classified Material

Security Classification Authority, CLASSIFIED BY:_____

Declassification or Downgrading Instructions, DECLASSIFY ON:_____
DOWNGRADE ON:_____

7. Attached will____will not____be presented to foreign nationals or presented at a symposium where foreign nationals or foreign representatives will be present. (If answer is "will" or "unknown", contact the Counterintelligence Office (Foreign Disclosure) for assistance.) (For Limited Distribution Only)

8. Name and address of periodical (if for journal publication):

_____

_____

_____Refereed _____Non refereed

9 Forum:_____

Title: _____

Location: _____

Date. _____

DoD sponsored: ___Yes ___ No

10. Attached has____has not____been coordinated with contractor. Name and address of contractor:

_____

_____

_____

11. Invention/work described herein has___ has not____been forwarded to Office of the Chief Counsel, CBDCOM.

Name of Inventor _____

Organization _____

Title Number of Invention _____

12 Portion of attached was __ was not__ extracted from copyrighted source.

Source Documentation: _____

Permission granted by _____

(Corresponcence Attached)

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-SP-88020

DECONTAMINATION OF CHEMICAL AGENTS GA, GB, GD, HD, L, AND VX A LITERATURE SURVEY (1918-1987)

Harvey W. Yurow, Ph.D.

RESEARCH DIRECTORATE

November 1988

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Destruction Notice

For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19, or DoD 5200.1-R, Information Security Program Regulation, Chapter IX. For unclassified/limited distribution documents, use the same standard as "*For Official Use Only*" material and destroy by any method that will prevent disclosure of contents or reconstruction of the document. When local circumstances or experience indicates that this destruction method is not sufficiently protective of unclassified limited information, local authorities may prescribe other methods but must give due consideration to the additional expense balanced against the degree of sensitivity.

Distribution Statement

Distribution authorized to U.S. Government agencies only because of test and evaluation; November 1988. Other requests for this document shall be referred to Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION / AVAILABILITY OF REPORT Distribution authorized to U.S. Government agencies only because of test and evaluation; (continued on reverse)
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-SP-88020	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION CRDEC 6b OFFICE SYMBOL (If applicable) SMCCR-RSL	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION CRDEC 8b. OFFICE SYMBOL (If applicable) SMCCR-RSL	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. C441. 03.4007 / WORK UNIT ACCESSION NO.

11 TITLE (Include Security Classification)
Decontamination of Chemical Agents GA, GB, GD, HD, L, and VX. A literature Survey (1918-1987)

12 PERSONAL AUTHOR(S)
Yurow, Harvey W., Ph.D.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Special Publication	FROM 88 Jan TO 88 Feb	1988 November	60

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
15	02		Decontamination, Chemical Agents, GB, GD, VX, Analysis, GA, HD, L

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report is an update and expansion of one published in 1981. Categories of decontaminants include water, strong bases, complexing agents and nucleophiles, oxidants thermal and irradiation techniques, physical collection, and bacterial and enzymatic methods.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☒ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL SANDRA J. JOHNSON	22b. TELEPHONE (Include Area Code) (301) 671-2914 22c. OFFICE SYMBOL SMCCR-SPS-T

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

3. DISTRIBUTION/AVAILABILITY OF REPORT (continued)

November 1988. Other requests for this document shall be referred to Commander, U.S. Army Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, MD 21010-5423.

PREFACE

This literature survey was authorized by the U.S. Army Toxic and Hazardous Materials Agency Task C441.03.4007, Agent Disposal Literature Survey. The initial report was begun in June 1979 and completed in August 1980. The updating was begun in January 1988 and completed in February 1988.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Acknowledgments

The author would like to thank Raymond E. Herd, Analytical Division, CRDEC, for a number of helpful discussions and Donna M. Jackson for preparing the draft for processing.

Blank

CONTENTS

DECONTAMINATION OF CHEMICAL AGENTS GA, GB, GD, HD, L, AND VX. A LITERATURE SURVEY (1918-1987)

1. INTRODUCTION

1.1 Purpose and Scope of Survey.

A literature survey was published in 1981 covering decontamination methods for the agents mustard (HD), isopropyl methylphosphonofluoridate (GB), and S-(2-diisopropylaminoethyl) methylphosphonothioate (VX) during the period 1918-1978.[1] The incentive for the current report was provided by a project in 1988 involving demilitarization of various chemical agents at Aberdeen Proving Ground, Maryland. Since the first survey, a number of novel techniques have been reported along with significant advances in older procedures. In addition, the analytical technology connected with these processes has become much more sophisticated and merits a separate section in the report. Because of interest in the agents ethyl N,N-dimethyl-phosphoramidocyanidate (GA), pinacolyl methylphosphonofluoridate (GD), and chlorovinyl dichloroarsine (L), their literature has been added to the survey. In all, 100 new references have been added.

Methods used for neutralizing a chemical agent will be strongly influenced by the amount of agent present and the environment in which the agent is present. Because there is no universal decontamination for each of the agents mentioned above, a listing is needed of all of the reported techniques that will serve for ordinary situations as well as a starting point for developing procedures for extraordinary situations.

This literature survey covers the period 1918-1987. Open literature publications, government reports, and industrial contract reports are included. Although the author has attempted to make this report all-inclusive, this goal cannot be obtained, and omissions have resulted. These omissions are not believed to be of a serious nature.

1.2 Background and Overview.

A large number of decontaminating systems or methods have been studied for the destruction of distilled HD, GB, GD, GA, VX, and L. These systems can be subdivided into several categories:

- water
- strong bases
- complexing agents and nucleophiles (other than 2)
- oxidants
- thermal methods

- irradiation techniques
- physical collection
- bacterial and enzymatic methods

In this report, each category will be considered in turn. Where reported, the following information (if available) will be included for each reference: quantity of agent processed, percentage destroyed, reaction kinetics, and method of analysis.

Those analytical methods that have been included in standard operating procedures (SOP) will be considered in detail in Section 9.

2. WATER

Both fresh and sea water, although plentiful and inexpensive, are relatively ineffective agents for the destruction of the chemical agents of concern in this report. Nevertheless, in locations where fresh and sea water are readily available, they have been used to wash contaminated surfaces.[2] The solubility of HD in water is low[3,4] (1 g/L), and the hydrolysis rate constant is relatively low (0.13 min^{-1}) at ambient temperature.[3] Mustard is 99.3% hydrolyzed at 50 °C in 100 min.[5] Increasing the temperature of the water,[6,7] or using steam,[8] causes volatilization of a portion of the HD.[9] Adding detergents (e.g., the alkyl sulfonates[10] or quaternary ammonium compounds) increases the solubility of HD 8-20 times but results in hydrolysis rates 3-20 times slower,[3] with polyglycol ethers, hydrolysis rates are doubled. A similar situation of decreased kinetics results when detergent micelles are used.[11] However, a 100-fold hydrolysis enhancement was reported for GD with the quaternary salt tetrapentyl ammonium bromide.[12] Enhanced kinetics were also obtained with 1-n-dodecyl-3-pyridinium aldoxime at pH 9.5 for GD and VX.[13] Similarly, film forming foams have also been investigated.[14]

The organophosphate GB is completely miscible with water while GA and GD are much less soluble (i.e., 100 g/L and 20 g/L, respectively).[15] The first two compounds hydrolyse fairly rapidly around neutral pH (i.e., half lives of 75 hr at pH 7 and 25 °C for GB and 175 min at 25 °C for GA in seawater).[16,17] The value for GD is 80 hr at pH 7 and 20 °C, too slow from a practical standpoint for decontamination.[15] Similarly, for VX, the values are 30 g/L of water (solubility) and 40 days at pH 7, respectively.[16]

Lewisite in water reacts rapidly to form lumps that are soluble only on prolonged stirring and are polymeric modifications of the oxide ClCH=CHAsO.[18] The aqueous solution of the oxide has vesicant properties.[19]

3. STRONG BASES

3.1 Aqueous Solution.

Strong bases in aqueous solution may be defined as those giving a pH of approximately 11 or greater. Cleavage rates for G agents and VX are proportional to the hydroxyl concentration; HD rates in basic solution are comparable to those in water alone.[11,20-22] Unfortunately, the higher pH solutions are more corrosive to skin and materials. Hydrolysis of GA, GB, and GD in strongly basic solutions involves the following equations.

$$C_2H_5OP[N(CH_3)_2](O)CN + 2\ NaOH = C_2H_5OP[N(CH_3)_2(O)ONa + NaCN + H_2O \quad (1)$$

$$i\text{-}C_3H_7OP(CH_3)(O)F + 2\ NaOH = i\text{-}C_3H_7OP(CH_3)(O)ONa + NaF + H_2O \quad (2)$$

$$C_6H_{13}OP(CH_3)(O)F + 2\ NaOH = C_6H_{13}OP(CH_3)(O)ONa + NaF + H_2O \quad (3)$$

The pseudo first-order rate constant for hydrolysis of GA was reported as being 0.02 min^{-1} at pH 9.5 and 25 °C. The heat of reaction for this constant was given as -10.1 kcal/mole.[23,24] In acidic solution, dimethylamine is formed. Toxic cyanide, formed in basic solution, is readily destroyed by hypochlorite with a rate constant of 2.67 x 10 M^{-1} sec^{-1} and an estimated heat of reaction of -215 kcal/mole, according to the following equation:[25]

$$2\ NaCN + 5\ NaOCl + 2\ NaOH = N_2 + 2\ Na_2CO_3 + 5\ NaCl + H_2O \quad (4)$$

For GB, the second-order reaction rate is 30 $M^{-1}sec^{-1}$, and the heat of reaction is -44.4 kcal/mole.[26] With 5% aqueous sodium hydroxide, the half life of GB is <0.8 s. The reaction rate of GD is comparable to that for GB with a reported half life at 20 °C of 0.08 hr in excess 5% aqueous sodium hydroxide.[15] The heat of reaction should be comparable to that given for GB because the same leaving group is involved. However, the lower aqueous solubility of GD as compared to GB necessitates the use of a mixed aqueous-organic solvent if the decontamination is not to be unduly prolonged in a heterogeneous system (Section 3.2).

With respect to VX, the pertinent equation is:

$$C_2H_5OP(CH_3)(O)SCH_2CH_2N(i\text{-}C_3H_7)_2 + 2\ NaOH = C_2H_5OP(CH_3)(O)ONa + NaSCH_2CH_2N(i\text{-}C_3H_7)_2 + H2O \quad (5)$$

The half life of VX at pH 14 is 1.3 min,[27] and the second-order rate constant is 30 M^{-1} hr^{-1}, but because of the relatively low agent solubility in water (above about 9 °C), the reaction requires a much longer time unless an organic solvent such as 2-methoxyethanol is included. Therefore, for VX (and HD), actual rates will be slower, depending upon the rate of solution of agent, which will depend in turn upon the degree of mixing of the heterogeneous systems.

Lewisite reacts with aqueous sodium hydroxide as follows:[18,28]

$$ClCH = CHAsCl_2 + 6\ NaOH = Na_3AsO_3 + 3NaCl + C_2H_2 + 3H_2O \quad (6)$$

The isomeric (cis and trans) L react at different rates in 16% aqueous sodium hydroxide with one isomer giving almost complete acetylene evolution in 2 min and the other requiring approximately 1 hr.[29] Because of the relative insolubility of L or its oxide in aqueous solution, use of a cosolvent such as alcohol is recommended. Analysis for residual L has presented certain problems (Section 9).

Many bases have been studied for decontamination. Whereas, the use of 10% aqueous sodium hydroxide has been reported to be effective against HD,[30] later reports indicated the opposite.[31,32] In another report, Reichert[33] found that 125-gal batches of HD could be effectively decontaminated with 125 gal of water at 70 °C, plus the addition of calcium oxide in excess, raising the temperature to 100 °C. The mixture was allowed to stand overnight, and analysis via thin-layer chromatography (TLC) and gas-liquid chromatography (GLC)-mass spectrometry (MS) indicated complete hydrolysis to thiodiglycol and calcium chloride, plus some polysulfide residue that separated. The author also mentions the use of aqueous sodium hydroxide and ammonium hydroxide for hydrolysis of HD, but there was no indication that these bases had been used for large-scale decontamination.

By contrast with HD, aqueous sodium hydroxide has been used as a standard method for decontaminating bulk GB from munitions. The reaction yields sodium isopropyl methylphosphonate and sodium fluoride and has been used for demilitarizing the M55 rocket[34] and M139 and E139 bomblets.[35] Once the GB has been hydrolyzed, the brine solution is dried prior to disposal. Much literature[36-50] has resulted for the testing for residual GB in the brine, in the drier emission, and in the dried salts. There are two standard methods for GB trace analysis, enzyme and GLC. Both require extraction of residual GB from the material of interest with a polychlorinated alkane. For the enzyme method[39] that is more sensitive but less specific and subject to more interference, the extract is usually subjected to a preliminary TLC separation[51] followed by scraping off the spot, reaction with cholinesterase, and by a pH, colorimetric or fluorometric measurement. The GLC procedure[49,51-53] is less sensitive but more specific (Section 9).

Because sodium hydroxide solutions produce hydrogen with the aluminum often accompanying the GB in munitions, less basic solutions have been investigated. One of these is aqueous sodium carbonate,[26,54] that is less corrosive for aluminum. In this solution, the half life of GB was reported to be 8.5 s with a first-order rate constant of 0.08 s^{-1} and a destruction

efficiency of >99.9999%. The heat of reaction (delta H) with 10% sodium carbonate has been estimated to be -22 kcal/mole. This was shown to give a "safe" temperature rise of 2.58 °C for an adiabatic process using 300% excess reagent (1 lb of GB/7 gal of 10% sodium carbonate). Methods of analysis were essentially the same as those for the determination of agent in hydroxide brines.

While it is more resistant to cleavage by bases than GB is, VX has been decomposed with aqueous sodium hydroxide.[55] Decontamination of 12.5 gal of VX by 150 gal of 10% sodium hydroxide required 6-8 hr with air agitation at 25-30 °C. This technique was recommended by Monsanto Research Corporation,[56] but the sulfur and nitrogen degradation products, including diisopropylaminoethanol, are not commercially reusable.

Similar studies were reported by the Navy.[57] Twelve and one-half gallons of VX was decontaminated using 150 gal of 10% aqueous sodium hydroxide (air agitated) in three stages (50-gal added at each stage). The solubility of VX was incomplete initially. The last two stages used heated sodium hydroxide solutions. The time for "complete" decontamination was 6-8 hr. The solubilization problem indicates that this method of decontamination will be unreliable unless the mixing process can be very adequately controlled.

It must also be noted that if the reacting VX contains the "Bis impurity," the action of base will generate a refractory compound (equation 7) that will not undergo further hydrolysis. This substance is highly toxic and will not pass Department of Transportation standards for transport to a disposal site.

$CH_3P(O)[SCH_2CH_2N(i\text{-}C_3H_7)_2]_2$ $\qquad$ $CH_3P(O)(ONa)SCH_2CH_2N(i\text{-}C_3H_7)_2$ (7)

"bis" analog of VX $\qquad$ toxic refractory anticholinesterase

Methods of analysis for residual VX in the brines and in the dried salts are similar to the methods for analyzing GB and involve extraction of agent followed by GLC (phosphorus and sulfur flame filters), or TLC with enzyme analysis.[16,58,59]

A newer method for VX involves conversion to a GB analog by reaction with silver fluoride followed by GLC.[49,50]

Sodium hydroxide also appears to be the decontaminant of choice for L. However, the residue contains inorganic arsenic that may present a disposal problem.

A number of other strongly basic sodium salts have been suggested[48,60,61] as substitutes for sodium hydroxide or sodium carbonate in decontamination, including trisodium phosphate or sodium silicate. But, these salts do not seem to have been studied in any detail.

Ammonia and other gaseous bases have been examined for agent destruction, as has a mixture of aqueous sodium hydroxide and 4-dimethylaminopyridine.[62,63]

3.2 Partly Aqueous and Nonaqueous Solutions.

The main advantage in working in these media is that the agent is usually more soluble and so should be more readily available for nucleophilic attack, other factors being equal. Yet, partially or completely nonaqueous solutions have lower dielectric constants than water and may slow the reaction. Also, there are often problems of toxicity and corrosivity connected with organic solvents. In the following examples, the substances have been used only for small-scale decontamination such as on skin, cloth, metal, or other surfaces.

Sodium sulfide, 15% in a mixture of glycercl, ethanol, and water, required 20 hr at an ambient temperature to destroy HD.[9]

Sodium hydroxide in methanol reacts too slowly with HD to be effective;[31] yet in ethanol, the half life is 11 hr.[32] While VX, like HD, is more soluble in alcoholic base, problems of flammability have lessened that decontaminant's use.[27] Steyermark[64] describes an effective skin decontaminant for HD consisting of a quaternary ammonium hydroxide or alkali metal hydroxide, alkoxide, or phenoxide in mixtures of dimethyl sulfoxide and water or alcohol. A mixture of 70% methyl cellosolve and 30% of a 50% aqueous sodium hydroxide solution[65] completely destroyed HD in 2 hr (verified by GLC) to yield thiodiglycol and sodium chloride. This agent has a relatively large capacity for HD decontamination and compared very favorably with other HD decontaminants. The agent is also valuable for decomposing a relatively water insoluble organophosphorus agent such as GD.

A number of multicomponent, strongly basic mixtures have been studied for decontaminating HD, GB, and VX. One of these mixtures is DS-2, consisting of 70% diethylenetriamine, 28% 2-methoxyethanol, and 2% sodium hydroxide, patented by Jackson[66] as being effective and relatively noncorrosive. With this mixture, the half lives for HD, GB, and VX [67,68] were 2.3 s, <30 s, and <7 s, respectively, at ambient temperature. The products formed from HD included divinyl sulfide, which is somewhat toxic, but much less so than HD. In one report,[67] 25cm^3 of HD plus 1.33 quarts of DS-2 gave a 31% yield of divinyl sulfide in a very rapid reaction. Residual HD was determined by GLC. Other studies on DS-2 were made by Day[69,70] with HD, cyclohexyl methylphosphonofluoridate [GF (a GB analog)], and VX on painted panels after standing overnight, and by Fielding[71] on various surfaces. Treatment was effective for GF and HD but somewhat ineffective for VX. The products from VX were tentatively identified as bis (2-diisopropylaminoethyl) disulfide,[66] presumably plus the O-ethyl methylphosphonic acid.

For G agents, the products are the same as those for hydrolysis in aqueous sodium hydroxide.

In work performed with DS-2 at Monsanto,[72] a thorough study was made on the function of the three components in the solution. It was assummed that the amine in DS-2 complexes with the sodium ion to give a superbase. Substitutes included crown ethers, polyethyleneimine and iminobis(propylamine). The 2-methoxyethanol in the standard DS-2 mixture was replaced as solvent by a variety of glymes in various formulations and the sodium hydroxide by lithium diethylamide. None of the substitute formulations was markedly superior to DS-2 that gave 100% HD destruction at an ambient temperature in several minutes. Unfortunately, DS-2, having a low sodium hydroxide content, has a relatively low decontaminating capacity. The compound is also corrosive to epoxy resins, neoprene, and wood.[60]

Another all-purpose decontaminant similar to DS-2 is the Air Force CD-1 (also known as APD) consisting of ethanolamine (55 vol%), 2-hydroxy-1-propylamine (45 vol%), and lithium hydroxide monohydrate (2.5 wt%). Initial tests on this mixture were favorable,[73,74] that is, rapid destruction of GB at 10:1 or 5:1 ratios (GLC analysis). However, later investigation showed this mixture to be inferior to DS-2 for HD,[66] particularly because of formation of the toxic product vinyl chloroethyl sulfide (half life of formation 10 min at ambient temperature). With CD-1 and GB at aerosol concentrations of 168 mg/L and 1,620 μg/L, respectively, Brody[75] found that 98% of agent was destroyed in 0.1 hr and >99% in 0.5 hr. When 1 wt% of VX was dissolved in CD-1, only 0.8% remained at 15 min (half life >2 min). For GB, the rate was even more rapid with only 0.06% remaining at 2 min.[75,76]

In studies on the reaction of VX with ethanolamine, with hexyleneglycol added to give homogeneity, Yurow and Davis found that 70% of the VX remained intact after 2.5 hr at room temperature.[57]

Studies by the Navy[77] were made of benzyltrimethyl-ammonium hydroxide in methanol as a decontaminant for small amounts of VX in the laboratory.

A solution of sodium hydroxide in dimethyl sulfoxide that functions as a superbase to convert HD rapidly to divinyl sulfide is similar to DS-2.[78]

Monoethanolamine (MEA), an organic solvent and relatively strong base, has been used for decontaminating HD in batches of 60 gal of HD with 30 gal of MEA.[32] Using MEA has a number of decided advantages,[79,80] including relatively high flash point, relatively nontoxic (TLV of 3 ppm), noncorrosive to metals, inexpensive, relatively stable, homogeneously reacts with HD, moderate heat of reaction, and requiring a volume ratio of only 5:1. The reaction of HD and MEA is given by equation 8.

$$(ClCH_2CH_2)_2S + 2HOCH_2CH_2NH_2 = HOCH_2CH_2\overset{+}{N}H(CH_2CH_2)_2S + HOCH_2CH_2\overset{+}{N}H_3 + 2Cl^- \quad (8)$$

The type of reaction represented by the above equation has received attention in the open literature,[57] but quantitative studies of products, kinetics, and thermochemistry were not reported. A decided advantage of these systems is the absence of inorganic salts in the final disposition process. The products from HD, that is, N-(2-hydroxyethyl)thiomorpholine hydrochloride, monoethanolamine hydrochloride, and small amounts of bis(hydroxyethylaminoethyl)sulfide, were incinerated at 900 °C to give carbon dioxide, hydrogen chloride, and various oxides of nitrogen and sulfur that were collected in an 18% aqueous sodium hydroxide scrubber.[32]

The half life of this reaction was reported as being 11 min at 57 °C and 40 min at 44 °C.[57] The heat of reaction at 50 °C was -40 kcal/mole. Above this temperature, the heat of reaction increased significantly, and cooling was required. With a 5:1 volume-to-volume (v/v) ratio of MEA to HD, the adiabatic temperature rises were from 50 °C (initial) to 113 °C (final) and from 65 °C (initial) to 151 °C (final).

Studies have indicated that for chloroform solutions of various agents, reaction with MEA may yield a delayed, violently exothermic reaction, especially in closed vessels. The hazard of a slowly appearing exotherm, that nevertheless results in a violent run-away reaction upon storage, is not an isolated instance in the history of stored materials resulting from disposal operations. Detailed methods and apparatus are being developed for safely eliminating the appearance of such unpleasant surprises.[57] Analysis of various systems are performed by computer-controlled adiabatic calorimetry with computer data-processing. Other approaches to the problem have been the previous use of differential thermal analysis (DTA) and differential scanning calorimetry (DSC), but the approach cited above develops much more complete information for analysis if an actual problem exists. However, detection of the problem should be adequately performed by DTA and/or DSC.

Analysis for MEA decontamination gave stack gas values (DB-3 method) of <0.03 mg/m^3 while brines contained <0.25 mg/L from starting batches of 60 gal of HD and 300 gal of MEA.[26] Several studies[79,80] led to the selection of MEA as a feasible decontaminant for the destruction of GB.[82] The compound has also been applied to destroying HD impregnated on charcoal (0.6 ppm after 8 days of stirring).[80] When combined with 4-(N,N-dimethylamino)-pyridine, MEA has been used for destroying GB.[81] However, warnings were given on explosions that involved MEA and the chloroform used as diluent for HD in identification kits.

Potassium oximates and phenoxides were evaluated as decontaminants in tetraglyme/dimethyleneglycol monoethylether.[83]

Methylamine (gaseous state) as well as ammonia have been examined for the decontamination of buildings.[84]

Superoxides in acetonitrile or dimethyl sulfoxide act as superbases with respect to HD simulants.[85,86]

3.3 Molten Salts.

In a novel technique for destroying chemical warfare agents, molten basic salts are used at elevated temperatures. In this method first studied by Atomics International,[87-89] HD, GB, and VX in air (feed rates of approximately 10 g/min) were passed through beds containing 90% sodium carbonate and 10% sodium sulfate at 1000 °C. The agents react according to equations 9, 10, and 11:

$$HD + 2Na_2CO_3 + 7O_2 = Na_2SO_4 + 2NaCl + 6CO_2 + 4H_2O \quad (9)$$

$$VX + 3Na_2CO_3 + 20.5O_2 = Na_3PO_4 + Na_2SO_4 + NaNO_3 + 14CO_2 + 13H_2O \quad (10)$$

$$GB + 2Na_2CO_3 + 6.5O_2 = NaF + Na_3PO_4 + 6CO_2 + 5H_2O \quad (11)$$

The bench scale results were: HD off-gas <0.023 mg/m^3, particulate filter <30 ng, melt residue <30 ng/g; GD off-gas <0.00049 ng/m^3, filter <50 ng, melt <100 ng/g; VX off-gas <0.000085 mg/m^3, filters <1.5 ng, melt <3 mg/g. These figures corresponded to agent destruction of 99.99999%.[90] Assay was by extraction followed by GLC-MS for GB and HD or by enzyme analysis for VX.

The molten salt method has several problems, including the presence of phosphorus pentoxide particulates, requiring efficient particulate filters, and the presence of sodium chloride condensation in off-gas lines, requiring low temperature for the molten salt.[91]

4. COMPLEXING AGENTS AND NUCLEOPHILES

4.1 Metallic Salts.

These compounds customarily are employed in solutions closer to neutrality than are the bases of Section 3 above and are frequently much less corrosive. Various metal ions have been observed to increase the hydrolysis rates of GB in water,[92-97] especially those of copper (II), uranium (VI), zirconium (IV), thorium (IV), and molybdenum (VI). Only a few of these systems have actually been translated into useful decontamination procedures. In one such procedure,[68] VX and GB on sateen were treated with 0.1-M uranyl nitrate and 0.1-M thorium nitrate solutions; neither was very effective. In another procedure[98] involving VX in solution, 95-98% of the agent was destroyed in 30 min with either zirconium (IV), nitrate, or copper (II) nitrate and tetramethylethylenediamine. Uranium (VI) dioxybis(5-sulfo-8-hydroxyquinoline) with a half

life for GB of 2.8 min at pH 10 and 24 min at pH 7 was also satisfactory.[99] Various metal salts, including mercury (II) perchlorate,[100] complex with HD without actually decomposing it. These salts have been used to impregnate clothing but are deactivated by perspiration.

Interest in decomposition of agents with metallic complexes has returned with investigations involving several promising compounds.[101-103] A complex involving cobalt, tetrasulfophthalocyanine, pyridine, and oxygen appears promising as does a complex of copper (II) and tetramethylenediamine that gave half life values at pH 7 of 0.2 min and 45 min for GD and VX, respectively.

4.2 Alpha Nucleophiles.

While hydroxide anion readily attacks electrophiles such as HD, GB, and VX, even more rapid reactions are given by various alpha nucleophiles although they are less basic. The enhanced reactivity is related to the presence of an unshared electron pair on the atom next to the one bearing the negative charge that decreases charge repulsion during interaction. Anions of hydroperoxides, hypochlorites, oximes, and hydroxamic acids with most of the reactions involving GB and VX are in this group.[92,104-108] While a number of these reactions have very favorable kinetics, as measured in the laboratory, only hypochlorites appear to have been used for large-scale decontamination and these properly fall under the heading of oxidants, which are considered below. In one report,[109] a mixture of sodium hypochlorite and sodium perborate was used for HD, but no rationale was given. In a hypothetical exercise,[27] a search was made for a hydroxamic acid that would decontaminate 400 g of VX from a munition by dissolution in 1200 L of a 0.2-M aqueous solution of the hydroxamic acid at pH 7-9, giving a final agent concentration of <30 µg/mL after 1 hr. The sought-after acid was not found. A number of promising alpha nucleophiles that react rapidly with diisopropyl phosphofluoridate, including a-oxominovaleronitrile, ethylenediaminetetracetohydroxamic acid, amylose oxime, and pentafluorobenzaldoxime have been synthesized by Reiner.[110]

Besides alpha nucleophiles, bidentate nucleophiles such as pyrocatechol and pyrogallol anions[111-115] hydrolyzed organophosphates rapidly. Here, too, promising results in the laboratory have not been turned into practical systems.

Sodium thiosulfate reacts rapidly with HD,[116] but neither this reaction nor one involving hydrolysis of GB at pH 7.6 in the presence of pyridinium bases has been applied to bulk quantities of agents.[117]

4.3 Micellar Nucleophiles.

Micellar nucleophiles are oximes containing a large aliphatic moiety that tends to concentrate on the surface of the solution where more favorable concentration effects should enhance organophosphate hydrolysis. As an example, the half life of VX was 40 sec in a pH 9.3 solution containing 0.001M of dodecylpyridinium-3-aldoxime iodide.[118] Recent studies have appeared on phase transfer catalysis for HD destruction.[119]

5. OXIDANTS

5.1 Halogen.

5.1.1 Calcium Hypochlorite.

Of the toxic agents under consideration in this report, HD and VX contain sulfur moieties that are readily subject to oxidation. One of the first substances[9] used for destroying HD was "bleach," which is normally found in three forms: a 5% aqueous sodium hypochlorite solution, chlorinated lime, a solid with the approximate formula CaClOCl and calcium hypochlorite (HTH) with the formula $Ca(OCl)_2$. The last named, having the highest percentage of available chlorine, is the form most often used for current decontamination.

The reaction of HTH with HD has been conducted in a variety of media.[30] With solid reagent, the reaction may be violently exothermic.[120] With hypochlorite in an aqueous slurry, the reaction is more easily controlled. This mixture has been recommended for the detoxification of buildings, ground, and other large-surface areas.[121-124]

While reaction varies with the proportion of reactants and temperature, the proposed equation[31] for the maximum consumption of bleach is:

$$(ClCH_2CH_2)_2S + 14\ OCl^- = SO_4^{2-} + 16\ Cl^- + 4CO_2 + 4H^+ + 2H_2O \quad (12)$$

With a deficiency of hypochlorite, the sulfoxide and/or the sulfone of mustard may be produced[125] with the former being relatively toxic.

As HD is relatively insoluble in water, the reaction with aqueous HTH is heterogeneous, and rates of decontamination have not been studied.[31] Nevertheless, several kinetic investigations have been made in dilute homogeneous solutions at various pH values.[126-127] In actually decontaminating HD with HTH,[128] scaled-down amounts corresponding to ratios of 11.7 lb of HD to 100 lb of HTH in 108 gal of water were stored for several days at an ambient temperature, treated with sodium thiosulfate to remove excess hypochlorite, and extracted with hexane. The extracts were submitted to GLC with a sensitivity

of 1 ppm of HD in hexane, and results indicated complete decontamination. The equation given for the reaction was:

$$(ClCH_2CH_2)_2S + 7Ca(OCl)_2 + 2Ca(OH)_2 = CaSO_4 + 8CaCl_2 + 4CO_2 + 6H_2O \quad (13)$$

A bleach slurry completely decontaminated HD on U.S. Navy landing craft.[2]

HD is determined in bleach solution[49] by extraction and subsequent GLC (Section 9).

To speed up reaction, suspensions have been made of bleaching powder in organic solvents. One such solvent, carbon tetrachloride,[31] was superior to aqueous bleach paste but was still slow because of the heterogeneous nature of the reaction. In another solvent, 8% HTH in a mixture of 76% water and 15% chlorinated hydrocarbon with 1% alkylbenzenesulfonate emulsifier was used.[129] Reaction occurred at the phase interface and theoretically, the system could be improved by including a phase transfer catalyst.[27] Organic chlorinating agents, which are more efficient, are discussed below.

Calcium hypochlorite has also been applied to decontaminating VX. The reaction is shown by equation 14:[130]

$$VX + 9OCl^- + 7OH^- = C_2H_5OP(CH_3)(O)O^- + HN(i\text{-}C_3H_7)_2 + SO_4^{2-} + 2CO_3^{2-} + 9Cl^- + 5H_2O \quad (14)$$

The reaction is rapid with a half life of 1.5 min at pH 10. Calcium hypochlorite has been used for demilitarizing VX in the CAMDS Project at Tooele Army Depot (Tooele, UT) but was considered less effective than acid chlorinolysis because the pH is critical and high-toxicity products can be formed if the pH drops to a value below 11.[37]

The reaction is highly exothermic[57] with an experimentally determined value of -675 kcal/mole and a first-order rate constant of 0.01 s^{-1}. The rise in temperature can be calculated from equation 15;

$$\text{rise in degrees C} = (\text{moles VX})\ 175/\text{gal 10\% HTH} \quad (15)$$

Initial results obtained from extracting trace amounts of VX from hypochlorite gave poor recoveries.[131-132] The current analytical procedure[49] is much more satisfactory (Section 9).

The reaction of L with hypochlorite has been studied, but because of the relatively slow kinetics of oxidation to inorganic arsenic compounds, it offers no advantage over aqueous sodium hydroxide.[133]

Self-destructing HTH solutions to limit corrosion have been prepared with half lives of approximately 100 s. The

solutions are called ASH and SLASH,[134] contain citrate to remove excess active chlorine, and have been used for biological agents.

5.1.2 Sodium Dichloroisocyanurate.

Sodium dichloroisocyanurate monohydrate (Fichlor, DB-63) that possesses considerable aqueous stability and solubility (1 M/L) and has been used for laboratory-scale decontamination of VX is similar in action to HTH.[135] The compound was reported for destroying HD, GD, and VX on paint surfaces,[136] and the test results were compared with those for other decontaminating agents. As with HTH, the stability of sodium dichloro-isocyanurate in aqueous solution is pH dependent.[137] Because of its favorable characteristics relative to HTH, Fichlor may be preferred in certain applications.

5.1.3 Chloramine B, Chloramine T, and NBO.

Chloramines B and T are two other water-soluble, active chlorine compounds of interest. Compared to HTH, they have greater stability and less corrosiveness when applied to skin,[123,124] but being more expensive, are not recommended for large-scale operations. Theoretical studies have been made on N-chlorinated compounds by Pitman and co-workers.[138] Generally, the weaker the acidity of the NH base, the more stable the N-chloro compound. These compounds react readily with tertiary amines, and a number of them have been suggested as decontaminants for VX.[27] The products of reaction of chloramine B with HD include bis(2-chloroethyl) sulfoxide and the sulfilimine $C_6H_5SO_2N{:}S(CH_2CH_2Cl)_2$.[139,140] The proportion of the former increases with increasing water content.

An aqueous mixture containing 3-bromo-4,4-dimethyl-2-oxazolidinone (NBO) and cetyltrimethylammonium chloride in a bicarbonate/carbonate buffer has been studied for decomposing HD and VX as well as GD.[141] The solubility of NBO in the mixture is 0.14 M at 19 °C. A 0.01-M NBO solution containing 0.0034-M HD gave <1% HD (GLC) at 10 min (half life of 0.2 min). For VX and the reagent, at a 1:10 mole ratio, the half life of the VX was 0.2 min. Studies with GD (and by analogy GB) indicated that both hydrolysis and attack by reagent were occurring with an agent half life of 0.5 min at a 1:1 mole ratio. Unfortunately, stability problems in solution have prevented greater use of this decontaminant.[142]

5.1.4 Dichloramine B, Dichloramine T, DANC, and Other Water-Insoluble Active Chlorine Compounds.

This group of compounds is soluble in many of the solvents in which HD and VX are soluble. However, the compounds are unstable in varying degrees to sunlight and moisture.[143] The dichloramines have been applied in carbon tetrachloride

solution,[144] in salves[144] with inert solids such as kieselguhr or talc, or with alkali or alkaline earth carbonates or bicarbonates.[145]

Other examples for this group include N-chloro-saccharin,[27] N-chlorosuccinimide,[27] N-chloracetamide,[146] N-chlorophthalimide,[146] bis (2,4,6-trichlorophenyl)-dichlorourea,[147] and N-(2,3,6-trichlorophenyl) N-chlorobenzamide.[143]

Various other active chlorine compounds have been investigated.[148,149]

With N-chlorosaccharin, it was predicted[27] that at pH 8.6 in aqueous solution, the half life of VX would be 0.0001 s, but low water solubility, among other factors, prevented application of the compound.

One formulation that was used extensively in the past was DANC,[30,32] a 7% solution of 1,1-methylenebis(3-chloro-5,5-dimethylhydantoin)(S-210) in tetrachloroethane. Other formulations[31] include: S-210 (10.3%), tetrachloroethane (67.3%), barium hydroxide octahydrate (2.8%), Aristowax (1.6%), and S-210 (1%), tetrachloroethane (2.9%), Spar 201 (4%), water (7%), remainder oil. In aqueous solution, S-210 reacts with HD to give a sulfilimine derivative.[125] Because of the high toxicity of tetrachloroethane and its corrosive effect on painted surfaces and rubber, DANC has become obsolete.

5.1.5 Chlorine and Chlorine Dioxide.

Chlorine has been used as a large-scale decontaminant for VX based upon earlier laboratory studies (half life 1.2 min at pH 4).[150] In the actual procedure,[151] 100-lb batches of VX from munitions are dissolved in 1.5 N hydrochloric acid (1:3 v/v), and chlorine is added to a green color. Reaction is rapid and strongly exothermic. Samples are quenched with sodium hydroxide or sodium carbonate and extracted with dichloromethane. Residual agent (3 µg/L) is determined via fluorimetry,[152] TLC and an enzyme assay,[37] or GLC.[153] The destruction efficiency was 99.999999%. The reaction is:

$$VX + 3Cl_2 + 4H_2O = C_2H_5OP(CH_3)(O)OH + HO_3SCH_2CH_2N(i\text{-}C_3H_7)_2 + 6HCl \qquad (16)$$

Dicyclohexylurea from the dicyclohexylcarbodiimide stabilizer in the VX was also found among the products. The solution from the chlorinolysis was converted to drum-dried salts.[154]

Chlorine dioxide reacts with VX to give carbon dioxide, carbonyl sulfide, sulfate ion, phosphonic acid, and diisopropylamine.[155] As with chlorine, kinetics are very favorable, but the explosive nature of the gas would tend to preclude large-scale work. However, this gas and other exotic

gaseous oxidants have been evaluated for building decontamination.[84]

5.2 Other Oxidants.

An early oxidant used for destroying HD was potassium permanganate in acetone that was used for cleaning metallic instruments.[9] Neutral permanganate completely detoxifies (enzyme-assay) VX at a 20:1 molar ratio.[155] Some of the products were ethyl methylphosphonic acid, N,N-diisopropyl-formamide, sulfate ion, and gelatinous manganese dioxide that, along with unreacted permanganate, presented disposal problems. When VX was reacted with permanganate in highly basic solution, the products formed indicated that hydrolysis predominated over oxidation.[27]

Potassium peroxydisulfate, in combination with a silver ion catalyst, has been suggested for decomposing VX,[27] but no experimental work seems to have been done.

Peracetic acid gave unimpressive results with GB and VX on sateen swatches.[68]

Various free radical systems were studied for oxidation of HD, GB, and VX; but, the approach showed little promise.[156,157]

Novel oxidations of various chemical agents with organic iodo compounds have been reported in micellar and microemulsion media.[158-161] Thus, with 5-nitro-2-iodosobenzoate, hydrolytic half lives at pH 7-8 were 40 min and 2.2 min for VX and GD, respectively.

Ozone as a decontaminant has been the subject of several reports.[84,162]

6. THERMAL METHODS.

6.1 Noncatalytic Procedures.

Numerous thermal decomposition studies have been made on HD, GB, VX, and L. Those on HD were begun as far back as 1918.[163,164] But, the first comprehensive report was that of Williams in 1947.[165] Decomposition in nitrogen proceeded at a reasonable rate at 180 °C to give hydrogen chloride, ethylene, ethylene dichloride, dithiane, and 2,2'-dichloroethyldisulfide at 450 °C; HD was completely decomposed, and hydrogen sulfide and vinyl chloride were formed. Similar results were obtained by AiResearch Corporation at 335-400 °C.[166] Incineration of HD was studied by Brooks and Parker[167] at temperatures between 150-800 °C with residence times of 1.96-2.17 s with GLC analysis of the effluents. Destruction of HD was essentially complete (99.9999%) at 500 °C with formation of hydrogen chloride and sulfur dioxide. Various other studies on the incineration of HD

gave similar results,[168-173] indicating that the method is effective. Complete combustion gives equation 16:

$$(ClCH_2CH_2)_2S + 6.5O_2 = 4CO_2 + SO_2 + 2HCl + 3H_2O \qquad (16)$$

The first study on the thermal decomposition of GB was made in 1954.[174] One reaction was run in a nitrogen atmosphere at 325-900 °C with a residence time of 0.15-4.0 s. Complete decomposition of GB to propylene and methylfluorophosphoric acid occurred at 560 °C. The best results were obtained at 650 °C and 2.7 s where the effluent had <1% biological activity. An open literature publication on the same subject was published in 1967.[175] The studies were extended to include incineration of GB in a work published by Pugh and co-workers.[176] With a temperature of 1300 °C and a residence time of 2.14 s, 99.9998% of the GB was decomposed. With scrubbing,[177] this value was increased to 99.99995%. A recent GB pyrolysis study was reported in 1985.[178] The hydrogen fluoride removal was 99.999%, but phosphoric acid mist was not removed because of the lack of a proper scrubber. Similar results were reported by Wynn[179] who found that at a feed rate of 7-13 lb/hr, 60-80% excess air, 1300 °C, a residence time of 1.96-2.14 s, and with a scrubber, GB was detoxified 99.999% as measured by enzyme assay. Incineration was also used to destroy GB in ID sets[172,174] with the reaction being:

$$2i\text{-}C_3H_7OP(CH_3)(O)F + 13O_2 = 8CO_2 + 9H_2O + P_2O_5 + 2HF \qquad (17)$$

The problem of phosphoric acid mist removal was addressed in a paper published in 1975.[180]

Thermal decomposition of VX has been reported in several papers.[166,181] At 350-435 °C, the products include 2-isopropyl-aminoethanethiol, O-ethyl-O-(2-diisopropylaminoethyl)-methylphosphonate and the "so called" sulfide and disulfide. Comprehensive studies on incineration of VX were made by Hildebrandt[182] and Sides.[183] At 1000-1100 °C, with a 0.25-s residence time, 10-45% excess air, and a VX feed rate of 0.1-0.2 g/min, destruction was 99.995%. With a propane flame and excess air at 700-800 °C and a 0.20-s residence time, destruction was 99.97%. Residual VX was determined via enzyme assay (equation 18):

$$2VX + 39.5O_2 = P_2O_5 + 2NO_2 + 2SO_2 + 22CO_2 + 26H_2O \qquad (18)$$

Later work with VX feeds of 7-15 lb/hr, 50-80% excess air, 1300 °C, a residence time of 1.79-2.11 s, and use of a scrubber gave destruction efficiencies of 99.999996% as assayed enzymatically.

Stack gas monitoring techniques for the above agents as well as automatic alarm[184] are considered with the analytical procedures in Section 9.

In addition to laboratory experiments involving the thermal decomposition of VX, various field trials have been performed for the destruction of this agent by heat.[185]

Incineration has also been applied to destroying L in chemical agent kits.[186] Conditions included a temperature of 632 °C, an oxygen excess of 119%, and a residence time of 4.7 s. However, problems were encountered in the analysis for residual L (Section 9).

Five extensive evaluations of thermal decomposition of chemical agents[186-190] as well as a recent literature review[191] have been published.

A relatively recent thermal method uses AC capacitative discharge decompositions,[192] and a corona discharge chemical reactor was effective for decomposing dimethyl methylphosphonate.[193]

6.2 Catalytic Procedures.

Thermal decomposition with catalysis is advantageous because generally, lower temperatures than those for noncatalytic procedures are required. A considerable amount of work in this field has been done by AiResearch Corporation.[167,194] Decomposition of GB occurred at 330-400 °C on reaction over a platinum catalyst on aluminum oxide. The resulting products were the same as those for combustion. But, as the catalyst became inactive, propylene and methylphosphonofluoridic acid were produced. During a 105-hr period, 160 g of GB was completely destroyed (IR analysis and rat biological test) by a 39.5-g catalyst at an initial concentration of1000-3000 ppm in air. For HD, the temperature range was 275-400 °C, and results with a residence time of 0.157 s gave 0 μ/L of air for HD (determined by GL). With VX, the figures were 9 mL destroyed completely in 43 hr (rat biological detection) at 400 °C when the catalyst was used.

Similar studies were made at Mine Safety Appliance Corporation[195] using a platinum on alumina catalyst for GB. The reaction was run at 400 °C with a residence time of 0.16 s for a flow rate of 500 μg of GB per liter of air. The reaction was stopped at 180 hr at which time GB in the effluent was 0.02 μg/L. The resulting products were fluorophosphoric acid, carbon dioxide, and water. Measurement of GB was made by the o-dianisidine procedure. A second catalyst described was ASC whetlerite, which was run at 50 °C and gave propene, carbon dioxide, water, and fluorophosphoric acid. The agent GB was completely destroyed at a flow rate of 500 μg of GB per liter of air for a 91-hr period.

Descriptions of catalytic investigations along the same lines were given by Philco Corporation.[196] Research in the Netherlands[197] was concerned with catalytic thermal

decomposition of GB on gamma-alumina, magnesium oxide, charcoal, and chromium trioxide on charcoal. These studies were more of a theoretical than practical nature.

7. IRRADIATION TECHNIQUES

Some work has been done using this approach. Both HD and VX contain sulfur atoms that are subject to oxidation. One system that has been proposed for VX involves cold aerial photooxidation with photosensitizers such as Rose Bengal.[27,198] The decays due to photolysis, hydrolysis, and oxidation in GB and VX clouds as they travel downwind have been reported.[199] A theoretical study has been published on the photochemical decomposition of various organophosphorus compounds at low temperatures encountered on winter battlefields.[200]

The effect of high intensity UV pulses on chemical agents have been published recently.[162,201]

Similarly, gamma radiation was applied for destroying chemical agents in munition casings.[202]

Decomposition of methylphosphonic difluoride was demonstrated with a CW, carbon dioxide, IR laser.[203]

The synergistic effect of irradiation combined with an oxidant (hypochlorite) decomposing the insecticide malathion was fivefold more effective than oxidant alone.[204] A similar effect was noted with organophosphorus insecticides and suspensions of zinc oxide and titanium dioxide semiconductors.[205,206]

8. PHYSICAL COLLECTION

Physical collection removes agent from one location to another without actually destroying it. This method is primarily of value for decontaminating surfaces or removing agent from water. Washing surfaces with water, water with detergent, or ethanol has been used for decontamination.[207]

Evaporation with forced air is another physical method that is of value for relatively volatile compounds.[208,209] This method is much less effective for high boiling compounds such as VX.[210]

An early method of physical collection involved adsorption of various toxic chemicals.[148] A more recent technique is that of reverse osmosis[211,212] for removal of GB and VX from water with cellulose acetate and polyamide membranes. Agent concentrations were significantly reduced.

Ion exchange resins have been used to remove small amounts of VX from hypochlorite brines,[131] but this was an analytical technique rather than a decontamination method. Amberlyte-15 resin (Rohm and Haas Corporation) was studied for

removing GB, VX, and HD from air.[213] Basic resins absorbed GB and possible hydrolytic products, then catalyzed the hydrolysis of GB.[214]

A review of ion-exchange methods reported for decontamination, with proposals for future work, was published in 1983. Ultra-fine resin-zeolite slurries as general-purpose, noncorrosive surface decontaminants and mixed-bed, cation-anion exchangers for potable water decontamination were among the recommendations.[215]

Aqueous charcoal slurries (23-28%) in water, plus corrosion inhibitors and antifreeze compounds, have been mentioned for decontamination.[60] In this connection, activated carbon also has been reported.[216]

9. BACTERIAL AND ENZYMATIC METHODS

Because of ecological considerations, these techniques have assumed greater importance. Thus, catalase was reported to catalyse the hydrolysis of GD (soman) and paraoxon but not that for VX.[217] The G17-2 marine bacterial strain degraded VX at an appreciable rate.[218] Within 30 min, squid DFPase gave 50% reduction of GB on painted surfaces.[219]

10. ANALYTICAL PROCEDURES FOR STANDARD DECONTAMINATION METHODS

The standard method for determining residual GB in an 18% sodium hydroxide solution requires initially adjusting the pH to 5 with dilute sulfuric acid and following this adjustment by extraction with chloroform, preconcentration of the extract using Chromosorb 106, and GLC analysis. The column type is DB-210, bonded-phase, fused silica capillary, 15-m long by 0.53-mm ID, with a 1-μm coated thickness of the stationary phase. The detector mode is phosphorus specific, and the detection limit is 6.3 ppb.[49] An identical procedure is used for determining GB in scrubber solutions and in sodium carbonate brines with detection limits of 4.8 ppb and 6.3 ppb, respectively. Gas chromatographic analysis of GB also has been reported using a DB5 megabore column 30 m by 1.5 μ (J&W Scientific) with a detection limit of 0.05 μg/mL of injected sample.[50]

A colorimetric technique for GB using o-dianisidine and perborate has a reported detection limit of 0.5 μg/mL; whereas, an autoanalyzer procedure using acetylcholinesterase and 5,5-dithiobis-2-nitrobenzoic acid claims a value of 0.25 ng/mL for the agent in an air stream.[50]

Analytical procedures also have been reported for GA and GD. Both chemical agents have been examined using GLC techniques. Retention indices have been determined,[153] MS patterns have been examined,[220,221] and collection efficiency on

porapak filters has been measured.[58] Sensitive colorimetric procedures include indole-pyrophosphate for GD (detection limit of 0.025 µg/mL) and 1-phenyl-3-methyl-5-pyrazolone for cyanide liberated from GA (detection limit of 0.025 µg/mL).[50]

The agent HD is determined in bleach solution according to the following procedure.[49] Excess bleach is neutralized with aqueous sodium arsenite, the end point being determined bipotentiometrically. Extraction is made with chloroform followed by preconcentration on Tenax-GC. The GC column is DB-210 bonded-phase, fused silica capillary, 15 m long by 0.53-mm ID, with a 1.0-µm coating thickness of the stationary phase. The detector is sulfur specific with a detection limit of 39.4 ppb.

The analysis of residual VX in hypochlorite requires an extraction prior to GLC. Initially, n-hexane was the extractant with a detection limit of 0.6 µg/mL, but recovery was poor.[131,132] The current method involves extraction with chloroform after a preliminary removal of excess hypochlorite with arsenite (HD analysis above) and increase of pH to 10.0. Preconcentration requires adsorption on Chromosorb 106 and conversion to a fluoro compound similar to GB by reaction with silver fluoride. The chromatographic column and detector are the same as those for GB, and the detection limit is 11.4 ppb.[49] A DB 608 column has been suggested for analyzing VX[50] as well as a DB5 megabore column (30 m, 1.5 µ, J&W Scientific) with a detection limit of 1 µg/mL for the latter.

Stack gas monitoring for HD involves collection on Tenax-GC, desorption and chromatography on a column of 10% OV-101 on 80/100 mesh Supelcoport in a teflon column, 6 ft by 0.085 in. ID, provided with a sulfur specific detector. The detection limit is 5 ng/L.[49] Porapak Q also has been evaluated for collecting HD.[222] Scrubber effluent analysis for the agent uses a similar procedure with a detection limit of 29.3 ppb. With a glass column (6 ft by 4-mm ID) packed with 10% QF-1 on 80/100 Chromosorb W-HP, the detection limit is 0.04 ng/mL of injected solution.[50] A colorimetric method uses an autoanalyzer and the DB-3 reagent, 4-(4-nitrobenzyl) pyridine, the detection limit being 0.04 µg/mL.[50,223]

Alternatives to GLC for determining HD have been proposed, including high-performance liquid chromatography.[224,225]

The current technique for stack gas monitoring of GB requires collecting Chromosorb 106 in a sampling tube. The column is a DB-1 bonded-phase, fused silica capillary 15 m long by 0.53 mm ID, with a 1.6-µm coating of the stationary phase. The phosphorus specific detector will indicate 0.4 ng/L of GB.[49] Beaded glass bubblers have been evaluated for GB sampling efficiency.[226]

The Automatic Continuous Air Monitoring System (ACAMS) alarm uses a GLC system to monitor air concentrations of GB and HD at chemical agent munitions disposal facilities[184,227] with detection limits of 0.0001 and 0.003 mg/m^3, respectively. Similarly, the Advanced Chemical Agent Detector/Alarm (ACADA) and Air Ionization Detector (AID) alarms use ionization detection principles.[228-230] The ACAMS unit has been modified to determine VX.[230]

There does not appear to be a standard method for stack gas monitoring of VX, but significant progress has been reported in this area.[59] Scrubber-effluent analysis for the agent is similar to that for bleach solution and uses a chloroform extraction, preconcentration, conversion to the fluoro compound, and chromatography on a DB-210 column. The detection limit is 2.64 ppb.[49] A sensitive colorimetric procedure for VX involves a molybdenum blue technique (0.25 μg/mL).[50]

A useful analytical procedure for determining residual GB, HD, and VX in solutions employing hydrolysis catalysts uses GLC/flame photometric detection (FPD).[231]

The analysis for residual L has presented significant problems with respect to detection limits and differentiation from the oxide. Results for detoxified chemical agent kits using a GLC procedure were sensitive only to 700 ppm [Analytical Division, U.S. Army Chemical Research, Development and Engineering Center (CRDEC), unpublished results]. By contrast, an indirect method measuring evolved acetylene by GLC analysis was sensitive to 70 ng, corresponding to 0.006 mg/m^3 for 120 L of gas sampled from an incineration process.[18] Similarly, determination by arsine in an atomic absorption technique is sensitive to 10 ng of the hydride, but results for bubblers were erratic.[188] However, L can be determined directly in air at a limit of 9 mg/m^3 by reaction with thio Michler's ketone as found in the M256 Chemical Agent Detector Kit.[232]

Several proposals have been made for the analysis of L in trace amounts. In one (E.W. Sarver, CRDEC, unpublished results, 1974), L is reacted with 1,2-ethanedithiol to give 2-(2-chlorovinyl)-1,3-dithioarsenole, which is submitted to GLC. Another proposal involves a preliminary separation by high-performance liquid chromatography coupled with amperometric assay with an estimated detection limit of 1 ppm (P. Bossle, CRDEC, unpublished results, 1986). Preliminary studies have been made (S. Hallowell, CRDEC, unpublished results, 1986) of the titration of L with sodium 2,3-dimercapto-1-propanesulfonate and a sulfide electrode.

In connection with demilitarization operations, dosimeters have been described in the literature for HD and GB.[233,234]

A comprehensive review was made comparing the available analytical techniques for detecting trace amounts of toxic materials at waste sites.[235]

11. COMPARISONS REPORTED AMONG VARIOUS DECONTAMINATION METHODS

There have been an appreciable number of comparison studies reported for destruction of bulk agent and for small amounts present (e.g., in identification kits).[227,236-246] In addition, cluster analysis has been applied to decontaminants.[247] Also of interest are the results of various ecological studies for demilitarization facilities.[248-250]

LITERATURE CITED

1. Yurow, H.W., Decontamination Methods for HD, GB, and VX, A Literature Survey, ARCSL-SP-80032, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, April 1981, UNCLASSIFIED Report.

2. Fielding, G.H., Johnson, J.E., and Krynitsky, J.A., Decontamination of Landing Craft at San Jose Island, Naval Research Laboratory Report No. P-2914, Naval Research Laboratory, Washington, DC, July 1946.

3. Herriot, R.M., and Anson, M.L., Effect of Detergents and Related Compounds on the Solubility and Rate of Solution of RHS, OSRD 653, NRDC Series 275, Office of Scientific Research and Development, National Defense Research Committee, June 1942.

4. Georgens, T., Solubility of HD, GB and VX, Test Report No. 2321-4-A/017/6, (Federal Republic of Germany) FSTC-HT-1315-78, January 1978, Foreign Restricted Report.

5. Holst, G., "Comparison of Pyridine, Ethyl Alcohol, Acetone as Solubilizing Agents," Acta. Chem. Scand. Vol. 12, p 1042 (1958).

6. Effectiveness for Decontamination of Hot and Cold Water with and without Detergents, Army Chemical Center Report on Test 689, Edgewood Arsenal, MD, December 1947.

7. Ross, C.M., Independent Evaluation Report (IER) for the Decontamination and Obscuration System (DOS) T114A, U.S. Army Chemical School Report, Fort McClellan, AL, 1986, UNCLASSIFIED Report.

8. Fielding, G.H., Decontamination of Ships. Operation Leroy, Naval Research Laboratory Report C-3240-70A/52CbM, Naval Research Laboratory, Washington, DC, May 1952.

9. The Cleaning of Objects Contaminated with Yperite, Chemical Warfare Service Report No. Z-197, Chemical Warfare Service, Washington, DC, May 1918.

10. Cante, C.J., Eachus, A.C., Delli Colli, H.T., and Stuempfle, A.K., Chemical Additives for Improved Surface Decontamination by Steam or Hot Water, ARCSL-TR-81028, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July 1981, UNCLASSIFIED Report.

11. Williamson, C.E., and Witten, B., Reaction of Some Nitrogen and Sulfur Mustards in Detergent Micelles, EATR-4490, Edgewood Arsenal, Aberdeen Proving Ground, MD, February 1971, UNCLASSIFIED Report.

12. Tadros, M.E., Bridger, K., Berrier, A., Hearns, R., and Woodbury, D., "Enhanced Hydrolysis of Diphenyl Chlorophosphate and Agent GD," In Proceedings of the 1986 CRDEC Scientific Conference on Chemical Defense, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

13. Sides, G.D., Dismukes, E.B., and Spafford, R.B., Evaluation of Decontamination Formulations, Contract No. DAAK11-77-C-0081, Southern Research Institute, Birmingham, AL, July 1981, UNCLASSIFIED Report.

14. Harvey, P.M., Sisson, R.M., and Wallace, V., Decontamination of Mustard Agent with Aqueous Film-Forming Foam, DPG-FR-87-006, Dugway Proving Ground, UT, February 1987, UNCLASSIFIED Report.

15. Tarantino, P.A., Master, I., and Decker, M.M., Composition of European Surface Waters and Aqueous Stability of Lethal Agents. A Literature Survey, ARCSL-TR-83023, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June 1983, CONFIDENTIAL Report.

16. Crabtree, E.V., and Sarver, E.W., Review of Analytical Procedures for GB, VX, and Their Degradation Products, EC-SP-76021, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, January 1977, UNCLASSIFIED Report.

17. Epstein, J., and Rosenblatt, D.H., Summary Report on a Data Base for Predicting Consequences of Chemical Disposal Operations, EASP 1200-12, Edgewood Arsenal, MD, January 1973, UNCLASSIFIED Report.

18. Valis, R.J., and Kolakowski, J.E., Development and Application of a Gas Chromatographic Method for Determination of Lewisite Emissions During Incineration of Obsolete Chemical Agent Identification Sets, ARCSL-TR-81092, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, December 1981, UNCLASSIFIED Report.

19. Green, S.J., and Price, T.S. "LVI. The Chlorovinyl-chloroarsines," J. Chem. Soc. Vol. 119, p 448 (1921).

20. Wilson, R.E., Fuller, E.W., and Schur, M.O., "Solubility and Rate of Hydrolysis of Mustard Gas in Water," J. Am. Chem. Soc. Vol. 44, p 2867 (1922).

21. Larsson, L., "The Alkaline Hydrolysis of Isopropoxy - Methyl - Phosphoryl - Fluoride and Some Analogs," Acta. Chem. Scand. Vol. 11, p 1131 (1957).

22. Epstein, J., Callahan, J.J., and Bauer, V.E., "The Kinetics and Mechanisms of Hydrolysis of Phosphonothiolates in Dilute Aqueous Solution," Phosphorus Vol. 4, p 157 (1974).

23. Larsson, L., "The Hydrolysis of Dimethyl-amidoethoxyphosphoryl Cyanide (Tabun)," Acta. Chem. Scand. Vol. 1, p 306 (1953).

24. Neale, E., The Thermochemistry of Organic Phosphorus Compounds. Part 3, Determination of Some Heats of Formation by Reaction Calorimetry and the Estimation of Bond Energy Terms, Porton Technical Paper No. 339, Porton Down, UK, November 1953, UNCLASSIFIED Report.

25. Gladysheva, A.I., Fedorina, G.N., Abliisova, I.G., Gus'kov, V.A., and Demidkina, T.A., "Mechanism of Kinetics and Oxidation of Cyanides by Active Chlorine," Uch. Zap. Tsentr. Nauchno Issled. Inst. Olovyannoi Promsti. Vol. 3(1969) Chem. Abstr. Vol. 76, p 28188 (1972).

26. Davis, G.T., Block, F., Gorrell, J.D., and Epstein, J., Fundamental Studies Related to the Decontamination and Disposal of GB-Filled Honest John Warhead Components, EC-TR-76101, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, March 1977, UNCLASSIFIED Report.

27. Davis, G.T., Demek, M.M., Gorell, T.G., Bates, J., Block, F., Sommer, H.Z., and Epstein, J., Search for a Noncorrosive Decontaminant for VX and for Application in Demilitarization Operations, ARCSL-TR-78028, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July 1978, UNCLASSIFIED Report.

28. Waters, W.A., and Williams, J.H., "Hydrolysis and Derivatives of Some Vesicant Arsenicals," J. Chem. Soc. p 18 (1950).

29. Bartlett, P.D., The Geometrical Isomers of M-1 (Lewisite), OSRD No. 470, Serial No. 211, Office of Scientific Research and Development, March 31, 1942.

30. Mankowich, K., Butcosk, A.F., Robbins, R., Roberts, W.B., and West, A.L., History of Research and Development of the Chemical Warfare Service through 1945. Decontamination of Chemical Agents, Part II, EASP-300-5-Pt-2, Edgewood Arsenal, Edgewood Arsenal, MD, September 1970, UNCLASSIFIED Report.

31. Block, F., and Davis, G.T., Survey of Decontamination Methods Related to Field Decontamination of Vehicles and Materiel, ARCSL-TR-79002, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, October 1978, UNCLASSIFIED Report.

32. Brankowitz, W.R., Demilitarization of Mustard Agent (HD) at Fort McClellan, Alabama, ARCSL-TR-77051, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, April 1978, UNCLASSIFIED Report.

33. Reichert, C., Study of Mustard Destruction by Hydrolysis, DRES-TN-329, Defense Research Establishment, Suffield Ralston, Canada, July 1975.

34. Edwards, B.A., Caustic Immersion Demilitarization of M55 Rocket Residue, DPG-SS-C130A, U.S. Army Dugway Proving Ground, Dugway, UT, February 1974.

35. Mohammed, A.M., Demilitarization of M139 and E139 Bomblets at Dugway Proving Ground, Utah. Use of Sodium Hydroxide Solution, DPG-FR-C150B, U.S. Army Dugway Proving Ground, Dugway, UT, April 1978.

36. Davis, P.M., Brooks, M.E., Mason, T., and Sass, S., Chemical and Thermal Methods for Analysis of GB Demil Brines and Spray Dried Salts, EC-TR-76079, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, February 1977, UNCLASSIFIED Report.

37. Thomas, G.W., Demil Plan Operation of the CAMDS at Tooele Army Depot, Inclosure No. 10, Agent Destruction System Testing and Reliability Data, DRCPM-DRD-TR-72015, March 1977.

38. Rinehart, D., The Determination of GB Emissions from Rocky Mountain Arsenal M34 Spray Drier, ARCSL-TR-77031, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, December 1977, UNCLASSIFIED Report.

39. Hess, T.L., An Automated Method for Measurement of Nanogram Quantities of Organophosphorus Poisons, U.S. Army Environmental Health Agency, Edgewood Arsenal, MD, November 1970, AD No. 717558.

40. Tomlinson, D.H., and Feller, H.L., Improved Automated Analysis for Nanogram Quantities of Organophosphorus Agents GB and VX, ED-TR-76045, Edgewood Arsenal, Edgewood Arsenal, MD, May 1976, UNCLASSIFIED Report.

41. Belcher, D.W., "Spray Drying of War Gas Residues," Chem. Eng. Prog. Vol. 73, p 101 (1977).

42. Gilson, N.C., Rapid Sensitive Gas-Liquid Chromatographic Methods for Analysis of HD, GF, and VX (U), Defense Research Establishment, DREO-693, Ottawa, Canada, June 1974, RESTRICTED Report.

43. Epstein, J., Davis, G.T., Demek, M.M., Eng, L., Gorrell, J.D., Pistritto, J.V., Jones, J.T., Richmond, J.A., Sarver, E.W., Schiff, L.J., Block, F., Sommer, H.Z., and Daasch, L.W., On the Mechanism of GB Formation in Spray Drying of GB Contaminated Brine Solutions, EC-TR-76009, Edgewood Arsenal, Edgewood Arsenal, MD, November 1975, UNCLASSIFIED Report.

44. Taczak, W.J., The Detection and Tracking of Stack Effluent with a Forward Looking IR Image Sensor, NSWC/DL-TR-3313, Naval Surface Weapons Center, Dahlgren, VA, June 1975.

45. Barrett, J.W., Investigation of Contamination from C-Agent Demil Plants and Determination of Effects on Real Time C-Agent Detection System, SORI-EAS-75-417, Southern Research Institute Progress Report No. 8, Southern Research Institute, Birmingham, AL, September 1975.

46. Goodson, L.H., and Jacobs, W.B., Solution Sampling Enzyme Alarm Studies (Spray Drier Studies) Analytical Chemistry, Contract No. DAAA15-74-C-0069, Midwest Research Institute, Kansas City, MO, 1 December 1975.

47. Ludemann, W., and Sass, S., Detection and Identification of Chemical Agents Using Spot Tests in Conjunction with TLC (U), EC-TR-75062, Edgewood Arsenal, Edgewood Arsenal, MD, November 1975, CONFIDENTIAL Report.

48. Fisher, T., Steger, R.J., Parker, G.A., and Sass, S., Gas-Chromatographic Methods for Analysis of Trace Quantities of GB and Associated Compounds (Demil of Effluent, Brine, Dried Salts, Munition Exudates), EC-TR-76080, Edgewood Arsenal, Edgewood Arsenal, MD, September 1976, UNCLASSIFIED Report.

49. Smith, J.E., Analytical Methods Development. Vol. 2. Standing Operating Procedures, Contract No. DAAK11-82-C-0162, Southern Research Institute, Birmingham, AL, December 1985, UNCLASSIFIED Report.

50. Fleming, E.H., Summarization, Documentation, and Compilation of Current and Appropriate Procedures for the Chemical Analysis of CW Agents, Their Degradation Products and Selected Simulants, Contract No. DAAL03-86-D-0001C, Battelle Research Institute, Columbus, OH, August 27, 1987, UNCLASSIFIED Report.

51. Harris, J.M., De Bruin, K., Gebhart, J.E., Garrett, B.C., and Prociv, T.M., GB.NaOH Neutralization Mechanism and Analytical Procedures Evaluation, Contract No. DAAG29-81-D-0100, Battelle Research Institute, Columbus, OH, July 1982, UNCLASSIFIED Report.

52. McKinney, A.L., Rocket Disposal Program Study, M55-CD-08.M55, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, November 1985, UNCLASSIFIED Report.

53. Alden, C.J., Stack, H.F., and Garrett, N.E., Estimated Toxicity of Neutralized Salts With and Without Trace Amounts of Agent GB, Contract No. DAAG29-81-D-0100, Northrup Services, Incorporated, June 1982, UNCLASSIFIED Report.

54. Rinehart, D., and Deiner, A., Method of Analysis for Determination of Isopropyl Methylphosphonofluoridate (GB) in Carbonate Brines, EO-TR-77008, Aberdeen Proving Ground, MD, June 1977, UNCLASSIFIED Report.

55. Childers, C.D., Decontamination of Bulk Quantities of VX with NaOH-Aqueous Solution, Technical Memorandum W-15167, Naval Weapons Laboratory, Dahlgren, VA, August 1967.

56. Hedley, W.H., Richardson, G.A., Early, D.E., Moscowitz, C.M., and Rezuick, R.B., Disposal of Detoxified Chemical Agents, MRC-DA-476, Contract No. DAAA15-74-C-0073, Monsanto Research Corporation, St. Louis, MO, April 1977.

57. Yurow, H.W., and Davis, G.T., Decontamination and Disposal Methods for Chemical Agents. A Literature Survey, ARCSL-TR-81080, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, November 1982, UNCLASSIFIED Report.

58. Stutz, M., and Sass, S., Collection and Sampling of Materials and Preparation for Identification and Other Analysis, EC-TR-76091, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June 1977, UNCLASSIFIED Report.

59. Garrett, B.C., Moore, F.R., and Prociv, T.M., Development of Gas Chromatographic Verification Method for Analysis of Military Chemical Agent VX in Atmospheric Bubbler Samples, Contract No. DAAG29-81-D-0100, Battelle Research Institute, Columbus, OH, February 1982, UNCLASSIFIED Report.

60. Ashcroft, H.P., and Parker, D.T., Effect of Chemical and Biological Agents and Decontaminants on Equipment (U), DTC-71-713, Deseret Test Center, UT, 1978, SECRET Report.

61. Novkovich, S., and Vojinovich, M., Alkaline Reagents for Decontamination and Reactions with Military Chemical Agents, FSTC-HT-0301-86, Hem Pregl (Yugoslavia) 23(85) (1982).

62. Zamejc, E.R., Mezey, E.J., Hayes, T.L., Wetzel, D.K., and Garrett, B.C., Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase 2. Laboratory Evaluation of Novel Agent Decontamination Concepts, Contract No. DAAK11-81-C-0101, Battelle Research Institute, Columbus, OH, June 1985, UNCLASSIFIED Report.

63. Cowsar, D.R., Lewis, D.H., and Dappert, D.O., Development of Reactive Materials for Decontamination of Personal Equipment, Contract No. DAAK11-78-C-0111, Southern Research Institute, Birmingham, AL, July 1980, UNCLASSIFIED Report.

64. Steyermark, P.R., Composition for Decontaminating Chemical Warfare Agents, (W.R. Grace and Company), U.S. Patent 3,810,842, 14 May 1974, Chemical Abstract Vol. 81, p 137872C (1974).

65. Davis, P.M., Kipp, R.L., Brooks, M.E., and Duggan, M.L., Decontamination Solution for the Disposal of Identification and Training Sets, ARCSL-TR-79004, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, April 1979, UNCLASSIFIED Report.

66. Jackson, J.B., Development of Decontamination Solution DS-2, CWLR 2368, Army Chemical Center, Edgewood Arsenal, MD, April 1960, UNCLASSIFIED Report.

67. Davis, G.T., Block, F., Sommer, H.Z., and Epstein, J., Studies on the Destruction of Toxic Agents VX and HD by the All-Purpose Decontaminants DS-2 and CD-1, EC-TR-75024, Edgewood Arsenal, Edgewood Arsenal, MD, May 1975, UNCLASSIFIED Report.

68. Sturgill, R.A., and Sanders, R.M., Methods and Material for Personnel and Equipment Decontamination, Book 1, GB-67-2378-6.1, Contract No. DA18-035-AMC-279A, Final Report for Task No. 24 on Collective Protection Against CB Agents, Litton Industries, Beverly Hills, CA, November 1970.

69. Day, S.E., and Gendason, P., Laboratory Evaluation of the Decontaminating Effectiveness of DS-2 and STB Slurry Against Agents on Painted Metal, ED-TR-74057, Edgewood Arsenal, Edgewood Arsenal, MD, November 1974, UNCLASSIFIED Report.

70. Day, S.E., Keck, C.H., Schwartz, M., and Gendason, P., Laboratory Comparison on the Requirements for and Effects of Decontaminants on Alkyd and Urethane Paints (U), EASP-74028, Edgewood Arsenal, Edgewood Arsenal, MD, March 1975, CONFIDENTIAL Report.

71. Fielding, G.H, Field Decontamination Studies with Chemical Warfare Decontamination Solution DS-2, NRL-6191, Naval Research Laboratory, Washington, DC, December 1964.

72. Richardson, G.A., Development of a Physical Decontamination System, EACR 1310-17, Contract No. DAAA15-71-C-0508, Monsanto Research Corporation, St. Louis, MO, August 1972.

73. Dismukes, E.B., and Barrett, W.G., All Purpose Chemical Biological (CB) Decontaminant, Contract No. AF08-(675)-5410, Southern Research Institute, Birmingham, AL, June 1978.

74. Wolverton, B.C., Development of Noncorrosive, Nonflammable, Low Toxicity Decontaminant Solution for Bacteria and Organophosphorus Compounds (U), NWL Technical Memorandum No. W-40164, Naval Weapons Laboratory, Dahlgren, VA, December 1964, CONFIDENTIAL Report.

75. Brody, D.V., Dissemination of Decontamination Solutions as Aerosols, Contract No. AF08-(675)-5410, AFATL-TR-69-98, Southern Research Institute, Birmingham, AL, July 1969.

76. Demek, M.M., Quarterly Progress Report, Decontamination Research Section, Physical Research Division, Edgewood Arsenal, Edgewood Arsenal, MD, 24 April 1969.

77. Brumfield, J.L., and Rumuly, D.L., The Reaction of VX with Benzyltrimethylammonium Methoxide, NWL-TR-2513, Naval Weapons Laboratory, Dahlgren, VA, September 1970, CONFIDENTIAL Report.

78. Braude, G.L., A Study of Chemical Agent Protective Substances and Concepts for Percutaneous Protection, Report No. RES-64-113, Contract No. DA18-108-AMC-263(A), Bimonthly Progress Report, W.R. Grace and Company, Columbia, MD, September 1964.

79. Pistritto, J., and Eng, L., Research Investigations Concerning the Decontamination of H/HD in Toxic Gas Sets, Letter Report EACL 28, Edgewood Arsenal, Edgewood Arsenal, MD, March 1974.

80. Rosenberg, S., Detoxification of War Gas I.D. Sets Containing Charcoal Impregnated with Chemical Agent, AD-A042499, 1977.

81. Davis, P.M., and Sass, S., Incineration Studies of a Solution of Detoxified Mustard (HD) - Monoethanolamine (MEA) Waste, Letter Report, Edgewood Arsenal, Edgewood Arsenal, MD, December 1974.

82. Cowsar, D.R., Study of Reactive Materials for Development of New Protective Concepts, SORI-3808-4, Contract No. DAAA15-77-C-0015, Southern Research Institute, Birmingham, AL, January 1978

83. Casselman, A.A., Mah, R., and Bannard, R.A.B., The Effectiveness of Three Potassium Oximates and Potassium Phenoxide in Tetraglyme/Diethylene Glycol Monomethyl Ether Systems as in Vitro Decontaminants for Chemical Warfare Agents, DREO-905, Defense Research Establishment, Ottawa, Canada, August 1984, CONFIDENTIAL Report.

84. Albizo, J.M., Evaluation of Gases as Potential Decontaminants for Building Decontamination, ARCSL-TR-81102, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July 1982, CONFIDENTIAL Report.

85. Seiders, R.P., and Ward, J.R., Use of Superoxide as a Chemical Decontaminant, CRDC-TR-84056, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, October 1984, UNCLASSIFIED Report.

86. Kwan, A., Kenley, R.A., Winterle, J.S., and Mill, T., Reaction of Superoxide Radical Anion with Pentacovalent Phosphorus Esters, Contract No. DAAG29-82-K-0134, SRI International, Menlo Park, CA, May 1985, UNCLASSIFIED Report.

87. Yosim, S.J., Barclay, K.M., Darnell, A.J., Paulson, R.B., and Richards, W.L., A Feasibility Study for the Disposal of Neutralized GB by the A.I. Molten Salt Combustion Process, Contract No. DAAA15-74-C-0174, Modification P00003, Rockwell International Corporation, Thousand Oaks, CA, June 1975, UNCLASSIFIED Report.

88. A Feasibility Study of Disposal of War Gas ID and Training Kits by A.I. Molten Salts Combustion Process, Contract No. DAAA15-74-C-0174, Modification P00001, Rockwell International Corporation, Thousand Oaks, CA, February 1975.

89. Disposal of Obsolete War Gas ID and Training Sets by A.I. Molten Salt Combustion Process, Volumes I and II, Contract No. DAAA15-74-C-0146, Rockwell International Corporation, Thousand Oaks, CA, August 1976.

90. Dustin, D.F., Riordan, M., Vigus, E., and Wagner, A., Applications of Molten Salt Incineration to the Demilitarization and Disposal of Chemical Materiel, EM-TR-76099, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, February 1977, UNCLASSIFIED Report.

91. Kraybill, M., A Compendium of Molten Salt Combustion Studies, ARCSL-SP-77009, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, December 1977, UNCLASSIFIED Report.

92. Larsson, L., "Studies on the Chemical Reactivity of Organic Phosphorus Compounds," Sven. Kem. Tidskr. Vol. 70, p 405 (1958).

93. Wagner - Jauregg, T., Hackley, B.E., Lies, T.A., Owens, O.O., and Proper, R., "Model Reactions of Phosphorus - Containing Enzyme Inactivators, IV. The Catalytic Activity of Certain Metal Salts and Chelates in the Hydrolysis of Diisopropyl Fluorophosphate," J. Am. Chem. Soc. Vol. 77, p 922 (1955).

94. Courtney, R.C., Gustafson, R.L., Westerback, S.J., Hyytiainen, H., Chaberek, S.L., and Martel, A.E., "Metal Chelate Compounds as Catalysts in the Hydrolysis of Isopropyl Methylphosphonofluoridate and Diisopropyl Phosphonofluoridate," J. Am. Chem. Soc. Vol. 79, p 3030 (1957).

95. Epstein, J., and Rosenblatt, D.H., "Kinetics of Some Metal Ion Catalyzed Hydrolyses of Isopropyl Methylphosphonofluoridate (GB) at 25 degrees C," J. Am. Chem. Soc. Vol. 80, p 3596 (1958).

96. Gustafson, R.L., and Martell, A.E., "A Kinetic Study of the Copper (II) Chelate Catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate," J. Am. Chem. Soc. Vol. 84, p 2309 (1962).

97. Ploetze, E., "Problem of Defense Against Chemical Warfare Materials," Explosivstoffe Vol. 12, p 219 (1964).

98. Cogliano, J.A., and Braude, G.L., CW Agent Decontamination by Metal Salts and Organometallic Compounds, RES-69-61, Contract No. DA18-035-AMC-287(A), W.R. Grace and Company, Columbia, MD, December 1969.

99. O'Connell, J.J., and Kwan, C.S., Chemical Warfare Decontamination by Catalytic Hydrolysis, USAF Eglin Contract to Monsanto, AD 395943, February 1968.

100. Sharkley, L., Cogliano, J.A., Lard, E.W., and Braude, G.L., Research and Feasibility Studies on Clothing Decontamination, Report No. RES-69-31, Quarterly Progress Report No. 19, Contract No. DA18-035-AMC-287(A), W.R. Grace and Company, Columbia, MD, June 1969.

101. Ward, J.R., and Seiders, R.P., Inferring Relative Reactivity of Decontaminants Toward Chemical Agents from Simulants, CRDC-TR-84043, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, August 1984, UNCLASSIFIED Report.

102. Wilson, R.B., Burrows, W., Winterle, J.S., and Kwan, A., "Cobalt Phthalocyanine Based Decontaminants," In Proceedings of the 1985 Scientific Conference on Chemical Defense Research, CRDEC-SP-86007, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April 1986, UNCLASSIFIED Report.

103. Albizo, J.M., and Ward, J.R., "Hydrolysis of GD and VX by 0.05/0.10 M Copper (II) Tetramethylene Diamine (TMEN)," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, May 1987, UNCLASSIFIED Report.

104. Hackley, B.E., Plapinger, R., Stolberg, M., and Wagner-Jauregg, T., "Acceleration of the Hydrolysis of Organic Fluorophosphates and Fluorophosphonates with Hydroxamic Acids," J. Am. Chem. Soc. Vol. 77, p 3651 (1955).

105. Demek, M.M., Endres, G.F., and Epstein, J., "Hydroxamic Acid Catalyzed Hydrolysis," U.S. Patent 3,068,072, 11 December 1962, Chemical Abstract Vol. 58, p 10660 (1963).

106. Epstein, J., Bauer, V.E., Saxe, M., and Demek, M.M., "Chlorine Catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate (Sarin) in Aqueous Solutions," J. Am. Chem. Soc. Vol. 78, p 4068 (1956).

107. Swidler, R., Plapinger, R.E., and Steinberg, G.M., "The Kinetics of the Reaction of Isopropyl Methylphosphonofluoridate (Sarin) with Substituted Benzohydroxamic Acids," J. Am. Chem. Soc. Vol. 81, p 327 (1959).

108. Stolberg, M., Cross, D., and Steinberg, G.M., The Reaction of VE with Oximes and Hydroxamic Acids, CWLR 2285, Army Chemical Center, Edgewood Arsenal, MD, August 1959, UNCLASSIFIED Report.

109. Vogel, C.I.B., "A New Hypochlorite Preparation," Chem. Prod. Vol. 4, p 40 (1941).

110. Reiner R., "The Decontamination of Surfaces Contaminated with CW Agents and Detoxification of Agents Injected in Organisms," BMVG-FBWT-74-6, Bundesministerium Der Verteidigung Bonn (West Germany) Wehrtechnik, 1974.

111. Jandorf, B.J., Chemical Reactions of G Agent in Neutral Solution, Part II. Reaction with Mono and Polyphenols, MLRR 81, Army Chemical Center, Edgewood Arsenal, MD, September 1951, SECRET Report.

112. O'Neil, J.J., Wagner-Jauregg, T., and Stolberg, M.A., Isolation of Reaction Products of GB with Amines, Hydroxylamine and Catechol, MLRR 160, Army Chemical Center, Edgewood Arsenal, MD, February 1953, UNCLASSIFIED Report.

113. Higuchi, T., Molecular Catalysis and Interactions in Aqueous Solutions, University of Wisconsin Semiannual Report, Contract No. DA18-108-AMC-88(A), July 1963.

114. Epstein, J., Plapinger, R.E., Michel, H.O., Cable, J.R., Stephani, R.A., Hester, R.J., Billington, C., and List, G.R., "Reactions of Isopropylmethylphosphonofluoridate with Substituted Phenols," J. Am. Chem. Soc. Vol. 86, pp 3075 and 4959 (1964).

115. Epstein, J., Rosenblatt, D.H., and Demek, M.M., "Kinetics of the Reaction of Isopropyl Methylphosphonofluoridate with Catechols at 25 degrees C," J. Am. Chem. Soc. Vol. 78, p 341 (1956).

116. Benes, J., and Weidenthaler, P., "The Mechanism of the Reaction of Dichloroethyldisulfide with Sodium Thiosulfate," Chem. Zvesti Vol. 11, p 324 (1957), Chemical Abstract Vol. 51, p 16227 (1957).

117. Grochowski, J.W., Bukowski, E., and Lisowski, E., "Hydrolysis of DFP and Sarin in the Presence of Pyridinium Bases and Some of Their Oxides," Biul. Wojsk. Akad. Tech. Vol. 14, p 93 (1965), Chemical Abstract Vol. 65, p 3685 (1966).

118. Epstein, J., Kaminski, J.J., Bodor, N., Enever, R., Sowa, J., and Higuchi, T., "Micellar Acceleration of Organophosphate Hydrolysis by Pyridinium Aldoxime Type Surfactants," J. Org. Chem. Vol. 43, p 2816 (1978).

119. Harris, J.M., and McManus, S.P., Nucleophilic Decontamination Agents, Contract No. DAAG29-82-K-0181, Alabama State University, Montgomery, AL, October 1985, UNCLASSIFIED Report.

120. Lipscomb, A.G., "The Reaction Between 2,2'-Dichlorodiethyl Sulfide (Mustard Gas) and Bleaching Powder," Analyst Vol. 65, p 100 (1940).

121. Drager, H., "Destruction of Toxics in Industrial Establishments," Dragerhefte, p 2210 (1932).

122. Renwanz, G., "Detoxification of Buildings Contaminated with Mustard Gas (Bis(Chlorothyl)sulfide)," Gasmaske Vol. 7, p 1 (1935).

123. Weidner, D., "The Destruction of Mustard Gas," Gasschutz and Luftschultz Vol. 5, p 133 (1936).

124. van Giffen, H.J., and van Bronkhorst, W.A., "The Cleaning Up of Streets and Public Squares Contaminated with Mustard Gas," Pharm. Weekbl. Vol. 74, p 102 (1937).

125. Buswell, A., Price, C.C., and Bullitt, O.H., The Chemistry of Mustard Gas as a Water Contaminant, Informal Report 65, Section 9-3-2, National Defense Research Committee of the Office of Scientific Research and Development, August 1943.

126. Holst, G., "The Reaction of Bis (2-chloroethyl) Sulfide (also the Oxidation Products Sulfoxide and Sulfone) with Hypochlorite in Pyridine-Water Solution," Sven. Kem. Tidskr. Vol. 53, p 319 (1941), Chemical Abstract Vol. 36, p 6881 (1942).

127. Eskanow, K., and Jachlewski, Z., "Studying the Reaction of B,B'-Di-Chlorodiethyl Sulfide with Calcium Hypochlorite in Aqueous Solution," Biul. Wojsk. Akad. Tech. Vol. 83 (1975), Chemical Abstract Vol. 84, p 179476u (1976).

128. DF, Edgewood Arsenal, to P. Wagner, 21 July 1973, Subject: Analysis of HD in Aqueous HTH Solutions (Omnibus Program).

129. Letter, Edgewood Arsenal from R.J. Redd, November 1976, Subject: Report of Visit to West German Republic 18-22 October 1976.

130. DF, Edgewood Arsenal, from J. Epstein, 23 May 1973, Subject: Heat of Reaction of VX with Alkaline Bleach Solution.

131. Wagner, P., Omnibus Program, Demil Progress Report, Edgewood Arsenal, Aberdeen Proving Ground, MD, 21 October 1976.

132. Wagner, P., Omnibus Program, Demil Progress Report, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, 4 February 1977.

133. Buswell, A.M., and Price, C.C., The Chemistry of Certain Arsenical Chemical Warfare Agents as Water Contaminants, OSRD 4193, Office of Scientific Research and Development, June 26, 1944.

134. Fielding, G.H., Neihof, R.A., Echols, W.H., and Dimmick, R.L., Disinfection with Hypochlorite, Application to Clothed Men, Construction Materiels, and Electronic and Electrical Items, NRL Report 7067, Naval Research Laboratory, Washington, DC, 29 June 1970.

135. Hovanec, J.W., Davis, G.T., and Cannon, P.L., Studies Related to the Demilitarization of the M-55 VX-Filled Rocket, ARCSL-TR-81100, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, April 1982, UNCLASSIFIED Report.

136. Amos, D., Comparison of Fichlor and DS-2 Decontaminants Against Agents HD, GD, and VX and Alkyd and Aliphatic Polyurethane Paints (U), MRL-R-701, Materials Research Laboratory, Ascot Vale, Australia, 1974, RESTRICTED Report.

137. Shaw, K.B., and Miller, R.K., A Laboratory Investigation of Aqueous Formulations of Sodium Dichloroisocyanurate (CDB-63) and Supertropical Bleach (STB) as Chemical Agent Decontaminants (U), DREO-697, Defense Research Establishment, Ottawa, Canada, June 1974, CONFIDENTIAL Report.

138. Pitman, I.H., Daron, H., Higuchi, T., and Hussain, A.A., "Prediction of Chlorine Potentials of N-Chlorinated Organic Molecules," J. Chem. Soc. Section B., p 1230 (1969).

139. Benes, J., "Mechanism of the Reaction of Chloramine B with Bis (2-Chloroethyl) Sulfide," Collect. Czech. Chem. Commun. Vol. 28, p 1171 (1963).

140. Sartori, M., The War Gases, p 232, D. Van Nostrand, New York, NY, 1940.

141. Dismukes, E.B., Sides, G.D., Spafford, R.B., and Seiders, R., Evaluation of Decontamination Formulations, Contract No. DAAK11-80-C-0036, Southern Research Institute, Birmingham, AL, May 1982, UNCLASSIFIED Report.

142. Higuchi, T., Detergent Decontamination Research, Contract No. DAAK11-77-C-0098, Interx Research Corporation, Lawrence, KS, June 1980, UNCLASSIFIED Report.

143. Hill, A.E., Composition for Destruction of Mustard Gas, U.S. Patent 2,926,107, 23 February 1960, Chemical Abstract Vol. 54, p 13502 (1960).

144. Philipp, C., Rendering B',B'-Dichlorodiethyl Sulfide Innocuous, German Patent 557,081, 13 June 1928, Chemical Abstract Vol. 27, p 355 (1933).

145. Philipp, C., Rendering B',B'-Dichlorodiethyl Sulfide Innocuous, German Patent 590,796, 9 January 1934, Chemical Abstract Vol. 28, p 2433 (1934).

146. Philipp, C., Rendering B',B'-Dichlorodiethyl Sulfide Innocuous, German Patent 588,131, 12 November 1933, Chemical Abstract Vol. 28, p 1427 (1934).

147. Albert, T.J., and Pfansteil, R., Composition for Destruction of Mustard Gas, U.S. Patent 2,927,037, March 1960, Chemical Abstract Vol. 54, p 13503 (1960).

148. Mitchell, T.F., Gilchrist, M.F., Lindsay, R., Messick, M., and Scarborough, P., Decontamination of Chemical Agents on Skin, EATR 4781, Edgewood Arsenal, Aberdeen Proving Ground, MD, October 1973, CONFIDENTIAL Report.

149. Gilchrist, M.F., Summary of Study of Decontamination of VX Contaminated Fabrics Using M13 Decontamination Kit, EASP 1300-2, Edgewood Arsenal, Aberdeen Proving Ground, MD, November 1972, CONFIDENTIAL Report.

150. Bauer, V.E., Demek, M.M., Corey, G.G., and Epstein, J., Chlorination of VX in Dilute Aqueous Solution at 25 degrees C, CWLR 2231, Army Chemical Center, Edgewood Arsenal, MD, August 1958, SECRET Report.

151. Benson, J.H., Valis, R.J., Kramer, S.R., Heminger, D.M., Hildebrandt, H.F., and Berenthein, T.C., Laboratory and Pilot Scale Detoxification of VX in Acidic Media Using Chlorine Gas, EM-TR-73070, Edgewood Arsenal, Aberdeen Proving Ground, MD, May 1974, UNCLASSIFIED Report.

152. Basset, M.C., Herd, R.E., and Woolridge, A.L., Improved Method for Analysis of VX in Field Test Samples, EATR-4117, Edgewood Arsenal, Edgewood Arsenal, MD, July 1967, UNCLASSIFIED Report.

153. Sass, S., Parker, G.A., and Fisher, T.L., Identification of Chemical Agents by GLC Employing Retention Indices (U), EC-TR-76120, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, February 1977, CONFIDENTIAL Report.

154. Valis, R.J., and Vigus, E.S., Pyrolysis of Detoxified Agent Wastes, 2. Drum - Dried Salts From the Acid Chlorinolysis of VX, National Technical Information Services Report, AD-A045475, 1977.

155. Epstein, J., Rosenblatt, D.H., Kramer, D.N., Jonas, L.A., and Bauer, V.E., Annual Summary of Progress of the Defense Research Development-1967, EATM 143-2, Edgewood Arsenal, Aberdeen Proving Ground, MD, April 1969, UNCLASSIFIED Report.

156. Preis, S., Oser, Z., Serafin, S., Poling, J., and Podall, H.E., Study of Chemical Agent Decontamination System for Multipurpose Use, Contract No. DA18-108-AMC-203(A), Melpar, Incorporated, Falls Church, VA, June 1964.

157. Braude, G.L., Research and Feasibility Studies on Clothing and Decontamination, RES-70-41, Contract No. DA18-035-AMC-287(A), W.R. Grace and Company, Columbia, MD, September 1970.

158. Moss, R.A., Kim, K.Y., and Swarup, S., "Efficient Catalytic Cleavage of Reactive Phosphates by an o-Iodosobenzoate Functionalized Surfactant," J. Amer. Chem. Soc. Vol. 108, p 788 (1986).

159. Hovanec, J.W., Durst, H.D., and Ward, J.R., "The Catalysis of the Hydrolysis of GD and VX by Orthoiodosobenzoate in a Strongly Cationic Emulsion," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

160. Mackay, R.A., Longo, F.R., Knier, B.L., Durst, H.D., and Brunside, B.B., "Catalytic Hydrolysis of Phosphate Esters in Microemulsions," In Proceedings of the 1986 CRDEC Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

161. Katritzky, A.R., Duell, B.L., and Durst, H.D., "Synthesis and Catalytic Activity of Functionalized Aromatic Iodoso Derivatives, In Proceedings of the 1986 CRDEC Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

162. Snelson, A., Clark, D., and Brabets, R., Fluorocarbon/Ozone and UV Decontamination Concept, Contract No. DAAK15-85-C-0005, IIT Research Institute, Chicago, IL, October 1986, UNCLASSIFIED Report.

163. Hall, R.E., and Landover, R.S., Decomposition of Mustard Oil at Ordinary Pressure, EAL-265A, 14 October 1918.

164. Stoltzenberg, H., Apparatus for Burning of Mustard in Ground," Z. Gesamte-Schiess-Sprengstoffwes Vol. 26, p 135 (1931).

165. Williams, A.H., "The Thermal Decomposition of 2,2'-Dichlorodiethyl Sulphide," J. Chem. Soc., p 318 (1947).

166. Cheselske, F.J., Wheeler, A., Weller, S.W., Baier, R.W., Dutch, P.H., and Weiler, F.B., Study of Catalytic and Thermal Decomposition of Toxic Agents as Collective Protection Against CB Agents, Contract DA 18-135-AMC-279A, CB-67-2378-10.1 and 10.2., Garrett AiResearch Corporation, Torrance, CA, October 1970,

167. Brooks, M.E., and Parker,G.A., Incineration/Pyrolysis of Several Agents and Related Chemical Materials in ID Sets, ARCSL-TR-79040, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June 1979, UNCLASSIFIED Report.

168. Kessler, S., and Vriesen, C.W., Study of Conversion of Mustard Gas to Useful Products, E 83-76, Contract No. DAAA15-76-C-0046, Morton Thiokol, Incorporated, Chicago, IL, March 1976.

169. Sass, S., and Davis, P.M., Laboratory Studies on the Incineration of Mustard (HD), EATR-4516, Edgewood Arsenal, Aberdeen Proving Ground, MD, May 1971, UNCLASSIFIED Report.

170. Titt, R.A., Destruction of Mustard Gas by Burning, Porton Program 18/55, Porton Down, UK, 19 April 1955.

171. Brooks, M.E., and Davis, P.M., Demilitarization of Identification Kits by Incineration, ARCSL-77020, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June 1977, UNCLASSIFIED Report.

172. Barrett, W.J., Requirements and Techniques for Monitoring Process for Demil of Chemical Agent Identification Sets, SORI-3828-1, SORI-EAS-77157, Southern Research Institute, Birmingham, AL, April 1977, UNCLASSIFIED Report.

173. Sides, G.D., and Manier, M.L., The Pyrolysis of Bis(2-Chloroethyl) Sulfide (HD), Contract No. DAAK11-84-C-0028, Southern Research Institute, Birmingham, AL, 28 June 1985, UNCLASSIFIED Report.

174. Reeves, A.M., and Kurtz, M.C., Thermal Decomposition of GB, CRLR 393, Army Chemical Center, Edgewood Arsenal, MD, 3 August 1954, UNCLASSIFIED Report.

175. Baier, R.W., and Weller, S.W., "Catalytic and Thermal Decomposition of Isopropyl Methyl Fluoromethyl-phosphonate," Ind. and Eng. Chem. Process Des. Dev. Vol. 6, p 380 (1967).

176. Pugh, D.L., Baker, J.A., Gervasoni, T.R., and Hildebrandt, H.F., Incineration of GB and Containment of Gaseous Products, EATR 4463, Edgewood Arsenal, Edgewood Arsenal, MD, October 1970, UNCLASSIFIED Report.

177. Sass, S., Laboratory Assimilation of Scrubber Efficiency for Detoxification of GB Vapor, Task Force Eagle Report No. 17, April 1970.

178. Sides, G.D., and Manier, M.L., Pyrolysis of Isopropyl Methylphosphonofluoridate (GB), Contract No. DAAK11-84-C-0028, Southern Research Institute, Birmingham, AL, 8 October 1985, UNCLASSIFIED Report.

179. Wynne, D.J., Pilot Scale Incineration of GB and VX and Containment of Gaseous Products, EATR 4734, Edgewood Arsenal, Aberdeen Proving Ground, MD, May 1973, UNCLASSIFIED Report.

180. Runnion, K.N., and Wagner, A., Incineration of VX and GB with Emphasis on Phosphoric Acid Removal, EM-TR-75037, Edgewood Arsenal, Aberdeen Proving Ground, MD, April 1975, UNCLASSIFIED Report.

181. Lapp, R.R., and Schneider, C.J., Jr., An Investigation of Thermal Decomposition of Bis(2-Ethylhexyl) Hydrogen Phosphite and Agent VX as Vapor at Elevated Temperature, Cornell Aerolaboratory Report No. GM-1592-65, Contract No. DA18-108-CML-6628, Cornell Aerolaboratories, Cornell, NY, 31 May 1962.

182. Hildebrandt, H.F., Gervasoni, T.R., and Baker, J.A., Incineration of VX and Containment of Gaseous Products, EATR 4586, Edgewood Arsenal, Aberdeen Proving Ground, MD, March 1972, UNCLASSIFIED Report.

183. Sides, G.D., and Manier, M.L., Pyrolysis of O-Ethyl S-(2-Diisopropylaminoethyl)Methylphosphonothiolate (VX), Contract No. DAAK11-84-C-0028, Southern Research Institute, Birmingham, AL, 4 November 1985, UNCLASSIFIED Report.

184. Sides, G.D., Construction, Development, and Testing of an Automatic Continuous Air Monitoring System (ACAMS) for Use at the Chemical Agents Munitions Disposal System (CAMS), Contract No. DAAK11-77-C-0075, Southern Research Institute, Birmingham, AL, December 1982, UNCLASSIFIED Report.

185. Neale, E., and Sinclair, K., RESTRICTED title, CDE Field Trail Report 32, Porton Down, UK, July 1972, RESTRICTED Report.

186. Schultz, T.J., Daiga, V.R., Shah, J.K., Kuhn, T.J., and Hersch, C.A., Thermal Process Development, Phase 1 Report, Concept Development, Contract No. DAAK11-82-C-0056, Midland-Ross Corporation, Cleveland, OH, March 1983, UNCLASSIFIED Report.

187. Dustin, D.F., Garey, M.P., Sudar, S., and Yosim, S.J., Evaluation of Alternate Thermal Processes for the Disposal of Obsolete Chemical Munitions, Contract No. DAAK11-82-C-0054, Rockwell International Corporation, Thousand Oaks, CA, April 1983, UNCLASSIFIED Report.

188. Duggan, M.L., Pilot-Scale Incineration and Detection Interference Studies for the Disposal of Toxic Gas and War Gas Identification Sets, ARCSL-TR-78048, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May 1979, UNCLASSIFIED Report.

189. Meseke, E.L., and Herd, R.E., Small-Scale Pilot Incineration Feasibility Study of Chemical Agent Identification Sets, ARCSL-TR-78069, Aberdeen Proving Ground, MD, May 1979, UNCLASSIFIED Report.

190. Sides, G.D., Manier, M.L., and Spafford, R.B., "The Pyrolysis of VX, GB, and HD Trapped in Stainless Steel Reaction Vessels," In Proceedings of the 1985 Scientific Conference on Chemical Defense Research, CRDEC-SP-86007, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April 1986, UNCLASSIFIED Report.

191. Sides, G.D., and Spafford, R.B., Literature Review of Thermal Decomposition Studies of the Agents GB, VX, and HD, Contract No. DAAK11-84-C-0028, Southern Research Institute, Birmingham, AL, 28 September 1984, UNCLASSIFIED Report.

192. Fraser, M.E., Eaton, H.G., and Sheinson, R.S., "Initial Decomposition Mechanisms and Products of Dimethyl Methylphosphonate in an Alternating Current Discharge," Environ. Sci. and Tech. Vol. 19, p 946 (1985).

193. Lee, C.K., Varghese, K., Tavlarides, L.L., and Mukkavilli, S., "Modeling of the Electrostatic Corona Discharge Reactor, I. Simplified Model," CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

194. Makowski, J., Proposal for Mobile Demil Unit for M55 Rocket, Progress Report 10, Volume I, Contract No. DA18-035-279A, Task 34, AiResearch, Division of Garrett Corporation, Torrance, CA, 22 September 1967.

195. Milius, J.W., Advanced Collective Protection System Design Studies, Mine Safety Appliances Report 72-214, Contract No. DAAA15-71-C-0498, July 1974.

196. Feasibility Study of Catalytic Methods of Air Purification, Contract No. DA18-108-CML-6671A, Philco Corporation, Aeroneutronics Division, 26 August 1964.

197. Van Bokhoven, J.J.G.M., Kuiper, A.E.T., and Medema, J., "The Role of Heterogeneity in the Kinetics of a Surface Reaction, II. Kinetics of Decomposition of Isopropyl Methylphosphonofluoridate Adsorbed on Gamma-Alumina," J. Catal. Vol. 43, p 168 (1976).

198. Mill, T., and Gould, C.W., Oxidation of Sulfur and Amine Model Compounds, EC-CR-76050, Contract No. DAAA15-74-C-0150, Stanford Research Institute, Edgewood Arsenal, Aberdeen Proving Ground, MD, January 1976.

199. Bagley, F.D., Methodology Study Method for Arriving at Agent Decay Parameters as Cloud Travels Downwind, DPG-TR-A105D, Dugway Proving Ground, UT, June 1973.

200. Britton, K.B., Low Temperature Effects on Sorption, Hydrolysis and Photolysis of Organophosphonates, CRREL Report No. 86-38, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, December 1986, UNCLASSIFIED Report.

201. Asmus, J.F., Decontamination by Pulsed Visible and Ultraviolet Radiation, Contract No. DAAK11-83-C-0045, Maxwell Laboratories, Incorporated, San Diego, CA, October 1986, UNCLASSIFIED Report.

202. Disalvo, R., Kok, K.D., Lowry, L.M., and Pfau, J.P., Destruction/Immobilization of Chemical Agents by High-Level Gamma Fields, Contract No. DAAK11-82-K-0020, Battelle Research Institute, Columbus, OH, July 1983, UNCLASSIFIED Report.

203. Stanley, A.E., "Laser-Induced Chemistry of Methylphosphonic Difluoride," In Proceedings of the 1985 Scientific Conference on Chemical Defense Research, CRDEC-SP-86007, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April 1986, UNCLASSIFIED Report.

204. Pellenbarg, R.E., and Dotson, D.A, "Aqueous Oxidizers and Ultraviolet Radiation Synergism for Decontamination Applications," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

205. Gratzel, C.K., Jirousek, M., and Gratzel, M., "Accelerated Decomposition of Active Phosphates on Titanium Dioxide Surfaces," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

206. Rose, T.L., and Nanjundiah, C., "Accelerated Decomposition of DFP on Illuminated Semiconductor Particles," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

207. Commerford, G.E., Eggleston, L.A., and Yuill, C.H., Decontamination with Fire Fighting Equipment, AFAL-TR-67-108, Southwest Research Institute Contract No. AF08(635)-5711, Air Force Armament Laboratory, Eglin AFB, FL, September 1967.

208. Little, R.C., Evaporation Decontamination, Part 1. Concepts and Preliminary Relations, NRL-MR-4881, Naval Research Laboratory, Washington, DC, August 1982, UNCLASSIFIED Report.

209. Segers, D.P., and Spafford, R.P., "High-Temperature Agent Evaporation Various Air Velocities," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

210. Tomlinson, G.T., and Samuel, A.H., Literature Survey of Physical and Chemical Properties of Agents VX, GD, HD, and HL, Volume I, Contract No. DAAK40-78-C-0004, Battelle Research Institute, Columbus, OH, July 1980, UNCLASSIFIED Report.

211. Lindsten, D.C., and Des Roches, P.R., Decontamination of Water Containing Chemical and Radiological Warfare Agents by Reverse Osmosis, National Technical Information Services Report, AD-A046203, 1977.

212. Lindsten, D.C., "Decontamination of Water Containing Chemical Warfare Agents," In Proceedings of the 1986 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

213. Braman, R.S., Preparation and Evaluation of Non-Carbonaceous Solvents and Collective Protection Against CB Agents, CB-67-2378-4.1, Contract No. DA18-035-AMC-279, Garrett Corporation, Torrance, CA, April 1968.

214. Chasanov, G., and Epstein, J., "Ion Exchange Resins as Catalysts in the Decomposition of Sarin," J. Polym. Sci. Vol. 31, p 399 (1958).

215. Janauer, G.E., A Selective Review and Assessment of Potential Applications of Ion-Exchange Resins in Chemical Analysis, Protection and Detoxification, ARCSL-SP-81023, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, January 1983, UNCLASSIFIED Report.

216. Rehrmann, J., and Hildebrandt, H.F., GB Removal from Water by Activated Carbons Under Dynamic Flow Conditions, ARCSL-TR-80018, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July 1980, UNCLASSIFIED Report.

217. Liu, C., Qang, G., and Zhou, T., "Hydrolysis of Soman and Paraoxon by Catalase," AFMIC-HT-035-87, Trans. Inst. Pharmacol. and Toxicol., Academy of Military Medical Science, China, Vol. 6, p 206 (1985).

218. Orndorff, S.A., VX/TETRISO Degradation, Contract No. N00014-86-C-0647, Genex Corporation, Gaithersburg, MD, July 1987, UNCLASSIFIED Report.

219. Rajan, K.S., Mainer, S., Hoskin, F.C.G., Steinman, K., and Schmell, E., "Enzymatic Detoxification of Surface-Bound Soman (GD) and Sarin (GB)," In Proceedings of the 1985 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

220. Sass, S., Dolzine, T.W., and Fisher, T.L., Methane Chemical Ionization (CI) Mass Spectrometry (MS), 1. Comparison with Electron Impact (ED/MS) for Identification of G Agents and VX, EC-TR-76059, Edgewood Arsenal, Aberdeen Proving Ground, MD, June 1976, CONFIDENTIAL Report.

221. Fisher, T.L., and Sass, S., Chemical Ionization/Mass Spectrometry (CI/MS) of Phosphoramidates and Phosphonate Nerve Agents and Related Compounds, EC-TR-77026, Edgewood Arsenal, Aberdeen Proving Ground, MD, July 1977, CONFIDENTIAL Report.

222. Fowler, W.K., Solid Sorbent Samplers for Area Monitoring, Contract No. DAAK11-77-C-0087, Southern Research Institute, Birmingham, AL, February 1982, UNCLASSIFIED Report.

223. Miskelly, P.R., and Herd, R.E., Development of Method for Sampling Trace Amounts of Sulfur Mustard (HD) and Nitrogen Mustards HN-1 and HN-3 from Air Streams and Analysis by Autoanalyzer Using DB3 Colorimetric Technique, ARCSL-TR-80065, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, January 1981, UNCLASSIFIED Report.

224. Brooks, M.E., Bossle, P.C., Wasserman, M.B., Steger, R.J., and Lochner, J.M., Analysis/Evaluation of Water and Soil Samples from Ocala Florida, CRDC-SP-86006, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, March 1986, UNCLASSIFIED Report.

225. Bossle, P.C., Hallowell, S.F., Reutter, D.J., and Sarver, E.W., Analysis of 2,2-Thiodiethanol, a Water Soluble Alkyl Sulfide, in Aqueous Matrices, CRDC-TR-86003, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, December 1985, UNCLASSIFIED Report.

226. Herd, R.E., Bouck, J., Kolakowski, J.E., Miskelly, P.R., and Norris, G.G., Evaluation of The Sampling Efficiency of Beaded Glass Bubblers for Monitoring Isopropyl Methylphosphonofluoridate (GB) Emissions in Air, ARCSL-TR-82027, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May 1983, UNCLASSIFIED Report.

227. Maskarinec, M.P., Wise, M.B., and Buchanan, M.V., Technology Assessment for the Determination of Chemical Agent Vapors in Demilitarization Facilities, ORNL/TM-10346, Oak Ridge National Laboratory, Oak Ridge, TN, January 1987, UNCLASSIFIED Report.

228. Castleman, B.W., and Donehoo, R.F., Advanced Chemical Agent Detector Alarm (ACADA). Feasibility Studies. Ionization Detection Principles, Contract No. DAAK11-78-C-0118, Honeywell, Incorporated, Minneapolis, MN, April 1980, UNCLASSIFIED Report.

229. Blyth, D.A., and Harden, C.S., Classified Title, ARCSL-SP-80021, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, October 1980, CONFIDENTIAL Report.

230. Weinberg, D.S., Fabrication and Evaluation of Three ACAMS (Automatic Continuous Air Monitoring System) Units with VX Monitoring Capability, Contract No. DAAK11-82-C-0018, Southern Research Institute, Birmingham, AL, August 1984, UNCLASSIFIED Report.

231. Albizo, J.M., "A Direct Aqueous Injection GLC-FPD Method for Use in Monitoring the Hydrolysis of GD, VX and HD by Chemical and Biological Catalysis in Aqueous Decontaminants," In Proceedings of the 1985 Scientific Conference on Chemical Defense Research, CRDEC-SP-87008, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report.

232. Strauch, L.D., Gamson, R.M., Turner, R.B., Stroterhoff, H.L., Sullivan, M.P., and Sonneman, G.B., M-256 Chemical Agent Detector Kit, The Detection of Lewisite, ED-TR-76121, Edgewood Arsenal, Aberdeen Proving Ground, MD, March 1977, UNCLASSIFIED Report.

233. Fowler, W.K., and Miller, H.C., Study of Solid Sorbents for GB and Mustard Dosimeters, Contract No. DAAK11-77-C-0086, Southern Research Institute, Birmingham, AL, April 1980, UNCLASSIFIED Report.

234. Cammarata, V.N., and Stroterhoff, H.L., Chemical Characterization of an Impinger Bubbler for the Personal GB Dosimeter System, ARCSL-TR-79006, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, April 1980, UNCLASSIFIED Report.

235. Snyder, R.E., Schulte, B.E., Mangoba, L., and McHale, E.T., Research and Development of Hazardous/Toxic Waste Analytical Screening Procedures, Available Field Methods for Rapid Screening of Hazardous Waste Materials at Waste Sites, Contract No. DAMD17-78-C-8075, Atlantic Research Corporation, Alexandria, VA, June 1983, UNCLASSIFIED Report.

236. Chinn, K.S., Effectiveness of U.S. Standard and Nonstandard Decontaminants, and Decontamination Efficiency, DPG/TA-86/15, Dugway Proving Ground, UT, May 1985, CONFIDENTIAL Report.

237. Ross, R.H., Daugherty, M.L., Holleman, J.W., Pal, B.C., and Smith, L.H., Problem Definition Study of Agent VX: Demilitarization, Health Effects and Toxicology, ORNL/EIS-200, Oak Ridge National Laboratory, Oak Ridge, TN, July 1983, SECRET Report.

238. Moynihan, P.I., Compton, L.E., Dastoor, M.N., Houseman, J., and Kalvinskas, J.J., Safe Disposal Techniques for DOD Toxic Waste, Volumes 1-3, Contract No. NAS7-918, Jet Propulsion Laboratory, Pasadena, CA, August 1983, UNCLASSIFIED Report.

239. Jody, B.J., Chettur, G., Dihu, R.J., Schurger, M., and Snow, R.H., Development of Chemical Processes for Chemical Demilitarization, Contract No. DAAK11-82-C-0091, IIT Research Institute, Chicago, IL, May 1983, UNCLASSIFIED Report.

240. Grotta, H.M., Nixon, J.R., Zamecj, E.R., Carlton, H.E., and Gaughan, P.J., Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities, Phase 1. Identification and Evaluation of Novel Decontamination Concepts, Volume 1, Contract No. DAAK11-81-C-0101, Battelle Research Institute, Columbus, OH, February 1983, UNCLASSIFIED Report.

241. Bucci, R.J., and Meseke, E.L., Process Description and Compendium of Chemical Agent Identification Sets Disposal Program Studies and Reports, ARCSL-SP-81018, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, November 1981, UNCLASSIFIED Report.

242. Disposal of Chemical Munitions and Agents, National Research Council, Washington, DC, Contract No. DAAG29-82-C-0012, 1984, UNCLASSIFIED Report.

243. Brankowitz, W.R., Witt, M.E., Ursillo, J.A., and Pantleo, J.C., Disposal of Chemical Agent Identification Sets at Rocky Mountain Arsenal, Report No. DRXTH-IS-FR-83203, Volumes 1-3, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, August 1983, UNCLASSIFIED Report.

244. Jones, W.E., Mahannah, J., Sommerer, S., and Kitchens, J.F., Engineering and Development Support for General Decon Technology for the U.S. Army's Installation Restoration Program, Task 5, Facility Decontamination, Contract No. DAAK11-80-C-0027, Atlanta Research Corporation, Alexandria, VA, July 1982, UNCLASSIFIED Report.

245. Maupin, L.S., and Franke, D., Operation of the Drill and Transfer System (DATS) at Pine Bluff Arsenal, Report No. DRXTH-FS-FR-8112, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, August 1981, UNCLASSIFIED Report.

246. Mason, D.W., Lawler, T.E., Spafford, R.B., and Coleman, D.R., "Development of a Chemical/Biological Decontaminant," In Proceedings of the 1984 Scientific Conference on Chemical Defense Research, CRDC-SP-85006, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, June 1985, UNCLASSIFIED Report.

247. Little, R.C., An Examination of Selected Decontaminants Using Cluster Analysis, NRL-MR-6006, Naval Research Laboratory, Washington, DC, July 1987, UNCLASSIFIED Report.

248. Lemont, S., Tucker, R.C., and Frew, R.L., Remedial Investigation of Sudbury Annex, MA, Contract No. DAAK11-84-D-0002, Dames and Moore, Bethesda, MD, November 1986, UNCLASSIFIED Report.

249. Small, M.J., Soil Detection Limits for Potential Chemical Warfare Related Contaminants at Fort McClellan, AL, USAMBRDL-TR-8208, U.S. Army Medical Bioengineering Research and Development Laboratory, Ft. McClellan, AL, May 1983, UNCLASSIFIED Report.

250. Carnes, S.A., Coleman, P.R., Hillsman, E.L., Griffin, G.D., and Kornegay, F.C., M55 Rocket Disposal Program Study, M55-OD-7, Preliminary Assessment of the Public Health Impacts of M55 Rocket Disposal-Plant Operations, ORNL-6195, Oak Ridge National Laboratory, Oak Ridge, TN, November 1985, UNCLASSIFIED Report.

Blank

Distribution List 3

Names	Copies
Commander	
U.S. Army Chemical Research, Development and Engineering Center	
ATTN: SMCCR-DDE	1
SMCCR-HV	1
SMCCR-MSI	2
SMCCR-MU	1
SMCCR-NB	1
SMCCR-OPC (B. Eckstein)	1
SMCCR-OPF	1
SMCCR-OPP	1
SMCCR-OPR	1
SMCCR-PMI	1
SMCCR-PPC	1
SMCCR-PPI	1
SMCCR-PPP	1
SMCCR-RS	1
SMCCR-RSC	1
SMCCR-RSL	1
SMCCR-RSP	1
SMCCR-RSP-A (M. Miller)	1
SMCCR-RSP-P	1
SMCCR-RST	1
SMCCR-RST-C (Tox Info Ofc)	2
SMCCR-SF	1
SMCCR-SPD	1
SMCCR-SPS-T	2
SMCCR-ST	1
SMCCR-TDT (S. Lawhorne)	1
SMCCR-RSL (Dr. H. W. Yurow)	5
Aberdeen Proving Ground, MD 21010-5423	
Commandant	
U.S. Army Ordnance Missile and Munitions Center and School	
ATTN: ATSK-EI (Mr. Cranford)	1
ATSK-ME	1
ATSK-TX	1
Redstone Arsenal, AL 35897-6700	
Commander	
U.S. Army Missile Command	
Redstone Scientific Information Center	
ATTN: AMSMI-RD-CS-R/ILL Documents	2
Redstone Arsenal, AL 35898-5241	
Commander	
Anniston Army Depot	
ATTN: SDSAN-CS	1
Anniston, AL 36201-5009	
Commandant	
U.S. Army Chemical School	
ATTN: ATZN-CM	1
ATZN-CM-CC	1
ATZN-CM-CS (Deputy MLSO)	1
ATZN-CM-MLB	1
ATZN-CM-NC	1
Fort McClellan, AL 36205-5020	
Commander	
U.S. Army Aviation Center	
ATTN: ATZQ-CAT-CA-M (CPT P. McCLuskey)	1
ATZQ-D-MS	1
Fort Rucker, AL 36362-5000	
Commander	
Pine Bluff Arsenal	
ATTN: SMCPB-MM (Mr. Dunemn)	1
SMCPB-MME (L. Gossage)	1
Pine Bluff, AR 71601-9500	
Commander	
U.S. Army Electronic Proving Ground	
ATTN: STEEP-CT-F	1
Fort Huachuca, AZ 85613-7110	
Commander	
U.S. Army Chemical Activity	
ATTN: APCA-SPO (CPT Wojciechowski)	1
APO San Francisco 96305-0008	
Commander	
U.S. Army Science and Technology Center Far East Office	
ATTN: Medical/Chemical Officer	2
APO San Francisco 96328-5000	
AFDPRC/PR	1
Lowry AFB, CO 80230-5000	
HQ NORAD/NCCBN	1
Cheyenne Mountain AFS - STOP 4	
Peterson AFB, CO 80914-5601	
Director	
Office Environmental and Life Sciences	
Office of Under Secretary of Defense (R&E)	
ATTN: Mr. Thomas R. Dashiell	1
The Pentagon	
Washington, DC 20301-3080	

Director
Defense Intelligence Agency
ATTN: DT-5A (Mr. C. Clark) 1
Washington, DC 20301-6111

HQDA (DAMO-SWC) 1
WASH DC 20310-0430

HQDA (DAMI-FIT-S&T) 1
WASH, DC 20310-1087

Commander
Naval Sea Systems Command
ATTN: Code 55X25 1
Washington, DC 20362-5101

Commander
Naval Sea Systems Command
ATTN: Navsea 05R24 (Dr. Gloria Patton) 1
Washington, DC 20362-5101

Commander
Naval Medical Command
ATTN: MEDCOM-02C 1
Washington, DC 20372-5120

Commander
Naval Research Laboratory
ATTN: Code 6180 (Mr. Little) 1
Code 6182 (J. Shirley) 1
4555 Overlook Avenue, SW
Washington, DC 20375-5000

Commanding General
Marine Corps Research, Development,
and Acquisition Command
ATTN: Code SSCNBC 1
Washington, DC 20380-0001

HQ AD/YQO 1
/YQX 1
Eglin AFG, FL 32542-6008

USAFTAWC/TCO 1
Eglin AFB, FL 32542-6008

Commander
U.S. Army Infantry Center
ATTN: NBC Branch, Directorate of Plans 1
and Training (Bldg 2294)
Fort Benning, GA 31905-5273

Commandant
U.S. Army Infantry School
ATTN: ATSH-CD-CS-CS 1
Fort Benning, GA 31905-5400

Commandant
U.S. Army Infantry School
ATTN: ATSH-B, NBC Branch 1
Fort Benning, GA 31905-5410

Commandant
U.S. Army Infantry School
ATTN: ATSH-CD-MLS-C 1
Fort Benning, GA 31905-5800

Commander
U.S. Army Armament, Munitions and
Chemical Command
ATTN: AMSMC-ASN 1
AMSMC-IMP-L 1
AMSMC-IRD-T 1
AMSMC-ISE 1
AMSMC-SG 1
AMSMC-SFS 1
Rock Island, IL 61299-6000

Director
U.S. Army Materiel Command Field Safety
Activity
ATTN: AMXOS-SE (Mr. W. P. Yutmeyer) 1
Charlestown, IN 47111-9669

Commander
U.S. Army Combined Arms Center Development
Activity
ATTN: ATZL-CAP 1
Fort Leavenworth, KS 66027-5300

Commander
U.S. Army TRADOC Independent Evaluation
Directorate
ATTN: ATZL-TIE-C (Mr. C. Annett) 1
Fort Leavenworth, KS 66027-5130

Commander
U.S. Army Armor School
ATTN: ATZK-DPT (NBC School) 1
Fort Knox, KY 40121-5211

Commander
Lexington Blue Grass Army Depot
ATTN: SDSLB-AMP-C (M. Williams) 1
Richmond, KY 40475-5070

Commander
U.S. Army Natick Research, Development and Engineering Center
ATTN: STRNC-AC 1
Natick, MA 01760-5015

Commander
U.S. Army Natick Research, Development and Engineering Center
ATTN: STRNC-UE 1
STRNC-UMP 1
STRNC-US 1
Kansas Street
Natick, MA 01760-5017

Commander
U.S. Army Natick Research, Development and Engineering Center
ATTN: STRNC-W 1
STRNC-WES 1
STRNC-WS 1
STRNC-WTS 1
STRNC-WTT 1
Kansas Street
Natick, MA 01760-5018

Commander
U.S. Army Natick Research, Development and Engineering Center
ATTN: STRNC-IC 1
STRNC-ITF (Dr. R. Roth) 1
STRNC-ITP (Mr. R. Liable) 1
Kansas Street
Natick, MA 01760-5019

Commander
U.S. Army Natick Research, Development and Engineering Center
ATTN: STRNC-YC (P. McKay) 1
Kansas Street
Natick, MA 01760-5020

Commander
U.S. Army Materials Technology Laboratory
ATTN: SLCMT-OP (Dr. N. Schneider) 1
Watertown, MA 02172-0001

HQ AFSC/XTH 1
Andrews AFB, MD 20334-5000

Commanding Officer
Naval Explosive Ordnance Disposal Technology Center
ATTN: Code BC-2 1
Indian Head, MD 20640-5070

Commander
Detachment S
USAOG, Team III
Fort Meade, MD 20755-5985

Commander
U.S. Army Laboratory Command
ATTN: SLCSM-SE (Mrs. F. Liu) 1
Adelphi, MD 20783-1145

Director
U.S. Army Human Engineering Laboratory
ATTN: AMXHE-IS (Mr. Harrah) 1
Aberdeen Proving Ground, MD 21005-5001

Commander
U.S. Army Test and Evaluation Command
ATTN: AMSTE-TE-T 1
Aberdeen Proving Ground, MD 21005-5055

Director
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-OD-ST (Tech Reports) 1
SLCBR-SECAD (Dr. A. Gauss, Jr.) 1
Aberdeen Proving Ground, MD 21005-5066

Director
U.S. Army Materiel Systems Analysis Activity
ATTN: AMXSY-CR (Mrs. C. Horley) 1
AMXSY-GC (Mr. F. Campbell) 1
AMXSY-MP (Mr. H. Cohen) 1
Aberdeen Proving Ground, MD 21005-5071

Commander
U.S. Army Environmental Hygiene Agency
ATTN: HSHB-O/Editorial Office 1
Aberdeen Proving Ground, MD 21010-5422

Commander
U.S. Army Armament, Munitions and Chemical Command
ATTN: AMSMC-HO (A) (Mr. J. K. Smart) 1
AMSMC-QAC (A) 1
AMSMC-QAE (A) 1
Aberdeen Proving Ground, MD 21010-5423

Commander
U.S. Army Technical Escort Unit
ATTN: SMCTE-AD 1
Aberdeen Proving Ground, MD 21010-5423

Commander
S. Army Medical Research Institute
of Chemical Defense
ATTN: SGRD-UV-L 1
Aberdeen Proving Ground, MD 21010-5425

Director
Armed Forces Medical Intelligence Center
ATTN: AFMIC-IS 1
Building 1607
Fort Detrick, Frederick, MD 21701-5004

Commander
U.S. Army Medical Bioengineering Research
and Development Laboratory
ATTN: SGRB-UBG-AL, Bldg 568 1
Fort Detrick, Frederick, MD 21701-5010

HQ, U.S. Army Aviation Systems Command
ATTN: AMSAV-ES 1
AMSAV-DI 1
AMSAV-N 1
AMCPM-ALSE 1
AMCPM-ASE 1
AMCPEO-LHX 1
AMCPM-AAH 1
AMCPM-ASH 1
AMCPM-BH 1
AMCPM-CO 1
AMCPM-CH47M 1
AMCPM-AE 1
Federal Center, 4300 Goodfellow Blvd
St. Louis, MO 63120-1798

Director
U.S. Army Research Office
ATTN: AMXRO-CB (Dr. R. Ghirardelli) 1
PO Box 12211
Research Triangle Park, NC 27709-2211

Commander
U.S. Army Cold Regions Research and
Engineering Laboratory
ATTN: CECRL-RG 1
72 Lyme Road
Hanover, NH 03755-1290

Commander
U.S. Army Armament Research, Development
and Engineering Center
ATTN: SMCAR-AE (Dr. S. Morrow) 1
SMCAR-AE (Mr. R. Reagan) 1
SMCAR-AET-O (Bldg 355 North) 1
SMCAR-MS1 2
Picatinny Arsenal, NJ 07806-5000

Project Manager
Cannon Artillery Weapons Systems
ATTN: AMCPM-CAWS-A 1
Picatinny Arsenal, NJ 07806-5000

Director
U.S. Army TRADOC Analysis Command
ATTN: ATRC-WDB (L. Dominguez) 1
ATRC-WSL 1
White Sands Missile Range, NM 88002-5502

Commander
U.S. Army Scientific and Technical
Information Team, Europe
ATTN: AMXMI-E-CO 1
Box 48
APO New York 09079-4734

Commander
32D Army Air Defense Command
ATTN: AETL-CM (MAJ(P) M. L. Michelson) 1
APO New York 09175

Commander
3d Ordnance Battalion
ATTN: AEUSA-UH 1
APO New York 09189-2078

Commander
U.S. Army Security Affairs Command
U.S. Army Research, Development
and Standardization Group (UK)
ATTN: LTC C. C. Smith 1
Box 65
FPO, NY 09510-1500

HQ ASD/AESD 1
Wright-Patterson AFB, OH 45433-6504

FTD/TQTR 1
Wright-Patterson AFB, OH 45433-6508

AWAL/FIEEC
Wright-Patterson AFB, OH 45433-6553

AWAL/FIES/SURVIAC
Wright-Patterson AFB, OH 45433-6553

AAMRL/HET
Wright-Patterson AFB, OH 45433-6573

AAMRL/TID
Wright-Patterson AFB, OH 45433-6573

Commander
U.S. Army Depot Systems Command
ATTN: AMSDS-QA-V (Mr. Werke)
AMSDS-RE-S (Mr. Peart-Russell)
AMSDS-SF (T. E. Krietz)
Chambersburg, PA 27201-4170

Commander
Naval Air Development Center
ATTN: Code 60241 (D. Herbert)
Warminster, PA 18974-5000

Commandant
U.S. Army Academy of Health Sciences
ATTN: HSHA-CDH (Dr. R. H. Mosebar)
HSHA-CDS (CPT Eng)
HSHA-IPM
Fort Sam Houston, TX 78234-6100

HQ HSD/APL
Brooks AFB, TX 78235-5000

HQ HSD/YA
Brooks AFB, TX 78235-5000

HQ USAFSAM/VNC
Brooks AFB, TX 78235-5000

Commander
U.S. Army Dugway Proving Ground
ATTN: STEDP-SD (Dr. L. Salomon)
Dugway, UT 84022-5010

Commander
U.S. Army Dugway Proving Ground
ATTN: STEDP-SD-TA-F (Technical Library)
Dugway, UT 84022-6630

HQDA (DASG-PSP)
5109 Leesburg Pike
Falls Church, VA 22041-3258

Director
U.S. Army Communications-Electronics Comma
Night Vision and Electro-Optics Directorate
ATTN: AMSEL-NV-D (Dr. R. Buser)
Fort Belvoir, VA 22060-5677

Commander
U.S. Army Nuclear and Chemical Agency
ATTN: MONA-CM
7500 Backlick Road, Bldg 2073
Springfield, VA 22150-3198

Chief of Naval Research
ATTN: Code 441
800 N. Quincy Street
Arlington, VA 22217

Deputy Director
Marine Corps Institute
ATTN: NBC CD;CDD2
Arlington, VA 22222-0001

Administrator
Defense Technical Information Center
ATTN: FDAC
Cameron Station, Building 5
Alexandria, VA 22304-6145

Commander
U.S. Army Materiel Command
ATTN: AMCCN
AMCSF-C
5001 Eisenhower Avenue
Alexandria, VA 22333-0001

Commander
Naval Surface Weapons Center
ATTN: Code E4311
Code G51 (Brumfield)
Code H33 (B. Furchak)
Dahlgren, VA 22448-500

Commander
U.S. Army Foreign Science and Technology Center
ATTN: AIAST-CW2
220 Seventh Street, NE
Charlottesville, VA 22901-5396

Director
Aviation Applied Technology Directorate
ATTN: SAVRT-ATL-ASV
Fort Eustis, VA 23604-5577

Commander
S. Army Training and Doctrine Command
IN: ATCD-N 1
Fort Monroe, VA 23651-5000

HQ TAC/DRPS
Langley AFB, VA 23665-5001 1